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Canada Centre for Mineral and Energy Technology | Centre canadien de la technologie des minéraux et de l'énergie

SELECTIVE FLOTATION OF COMPLEX SULPHIDE ORES

PHASE I (WITH SPECIAL REFERENCE TO Cu/Zn)

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ABSTRACT

The physical and electrochemical factors that affect selectivity during the separation of complex sulphide minerals in general and that of Cu/Zn in particular are reviewed. Bench scale flotation tests were conducted to investigate the effects of the interactions of these factors.

Based on a literature survey, four depressants ($ZnSO_4$, SO_2, CaO, and cyanide) were identified as forming a basic reagent group required for selective depression of Zn and Fe in complex sulphide ores in general and in pyritic Cu/Zn ores in particular. This is supported by the results of tests conducted. They have been shown to play different roles in the flotation pulp and by varying their ratio it is possible to create conditions that activate chalcopyrite while maintaining sphalerite and pyrite depressed.

A Cu/Zn pyritic ore whose treatment poses a selectivity problem in an operating flotation plant was chosen for the test work. Multi-factor experimental designs were used to screen and investigate the most influential factors.

Aeration of flotation pulp, after grinding the ore in a rod mill with depressants and before collector addition was found to largely determine the overall metallurgy. Pulp potential was monitored at all stages of conditioning and flotation during the test. A strong correlation was found to exist between the potential just before collector addition and the selectivity of the sulphides against each other. The pulp potential, attained after 20 minutes pulp aeration, was found to strongly depend on the level and combination of the depressants used during grinding.

The study of conditions of maximum differential depression of Zn and Fe against Cu, regardless of the level of Cu recovery, indicated the existence of different combinations of the depressants which yielded similar levels of selectivity (at various recoveries). The best operating conditions were then identified by comparing results from those conditions which gave a high selectivity. A very high level of selectivity of chalcopyrite against sphalerite and pyrite was achieved, at an optimum Cu con grade and metal recovery, through the potential control of flotation pulp by aeration. Oxidizing the pulp to about -110 (mV; SCE) prior to collector addition allowed to obtain a high grade copper rougher concentrate (> 23% Cu) with low Zn content (<2.7%) at a Cu recovery higher than 87%. The recovery of Zn to the Zn rougher concentrate was higher than 89%. This is considered as a significant improvement of selectivity, because the concentrating plant produces a Cu concentrate with 23.4% Cu and higher than 5% Zn after double cleaning at significantly lower recoveries.

The process developed for this particular ore was then tested on another Cu/Zn ore (from a different origin) of a comparable head

grade. About 90% Cu was recovered at a rougher concentrate grade of 23.2% Cu and 2.4% Zn. Subsequently, 88% Zn was recovered to a rougher concentrate grading 40.5% Zn. Currently, the concentrator produces a Cu concentrate grading 25% Cu and 4-5% Zn after a triple cleaning. The Cu flotation scheme consists of roughing, regrinding, scavenging and triple cleaning. In view of this, the present process is believed to be of a techno-economic importance for Cu/Zn concentrators.

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1.0 INTRODUCTION

Selective flotation is a characteristic of many of the Canadian base metal concentrators. Very few of these concentrators are operating without any major selectivity problem. It is believed that the problem will become more and more serious as the ore to be processed, in the future, is generally becoming more refractive and lower in grade.

CANMET, through discussions with various concentrators, has identified four major areas of concern.

1. Flotation plants will require extra capacity to handle extra throughput that will be required to compensate for the reduced head grade. If the sulphide gangue (mainly pyrite) is selectively rejected at the early stage of flotation this may not pose a serious problem.

2. Most plants have to go through many flotation steps in order to achieve the minimum concentrate grade acceptable to smelters.

3. In many cases even after going through multiple concentrate cleaning stages, the loss of one metal to the concentrate of the other is just too high to be acceptable.

4. Some companies have or are intending to change the existing smelting technology that has allowed in the past the recovery of, for example, Zn from the Cu concentrate. In the new smelter it is no more possible to recover zinc and its presence in copper concentrate will be only a nuisance to the process.

In order to address these general concern of the Canadian concentrators, CANMET initiated this research project in June 1989. The short term objective of the project is:

- to review and publish the methods and practices as related to the art of selective flotation of complex sulphide ores with special reference to Cu/Zn.

- to conduct bench scale tests to identify the most appropriate procedures of selective flotation and methods to control selectivity of metals against each other .

The long term objective of the investigation is to develop a generalized selective flotation scheme and to test it on a pilot scale.

The problems associated with selective flotation or selective depression of complex sulphide minerals are very common. It is only in very rare cases that a sulphide concentrator operates without significant selectivity problems throughout the mine life. A small

change in the ore mineralogy may upset the selectivity, calling for more plant and/or reagent modifications.

The selectivity of sulphide minerals separation depends on the flotation chemistry used, particle size variations and the degree of particle liberation. The normal variables that are available for adjustment in selective separation process are pH (as controlled by lime or soda ash, SO_2 or H_2SO_4 etc.), level of aeration, pulp temperature, the type(s) of reagent(s) and their ratio(s).

In many instances middling recirculation in all circuits affects selectivity negatively, and the number of recirculation circuits in a given flotation plant is a direct indication of selectivity problem.

Other factors that affect selectivity are subsequent desorption of collectors from bulk floated concentrates. When the flotation rates of the minerals to be separated are very similar, the use of one or more depressants or modifiers such as cyanide, SO_2, NaSH, $ZnSO_4$, Na_2SO_3, etc. is required. Controlled oxidation of the pulp with air or other oxidants also permits a good separation between sulphides.

Cyanide in an alkaline medium (lime or soda ash) is one of the commonly used depressants for sphalerite and pyrite. In most cases the depression mechanism is very effective but, there are also cases where the addition of cyanide increases the amount of zinc reporting to the Cu/Pb bulk concentrate (7). In general it has the reputation of causing a permanent depression of sphalerite, pyrite, pyrrhotite and pentlandite, but only temporary depression of chalcopyrite. This temporary depression of chalcopyrite should always be taken into account.

In some cases the chemical used to control the pulp pH, whether lime or soda ash has no significant effect on sphalerite and pyrite depression during Pb/Cu bulk flotation (7), but in other cases the effect of one is decisively more pronounced than the other. Repeated attempts to replace soda ash with the cheaper lime in the Brunswick Cu/Pb circuit resulted in the deterioration of selectivity and loss of Ag, Pb. Relative to lime soda ash drastically improved the grade and recovery of both Pb and Zn in the Anvil concentrator operated by Cyprus at Faro in the Yukon (15).

Depression of zinc minerals during selective flotation of sulphide ores is usually not a problem; controlling pyrite flotation is sufficient to keep sphalerite depressed. A more difficult task, however, is depressing a preactivated zinc mineral, whose floatability is similar or even more pronounced than that of copper or lead minerals. The general approach to treating such ores is to find a combination of depressants for zinc which is also an

effective depressant for pyrite and pyrrhotite but does not cause chalcopyrite depression.

Observation of different flotation plant flowsheets and results of numerous tests undertaken by different laboratories on Cu/Zn separation indicated that no flowsheet that could constitute a general ore treatment scheme to achieve a definite selective separation exists. Fundamental factors which make each ore treatment scheme unique are: feed grade, liberation size of valuable components and their intergrowth, and other components of flotation pulp including reagents, cations and anions in the process water, dissolved oxygen, products from grinding media, secondary mineral surface products.

It is also extremely difficult to predict theoretically which component- chemical, physical or material interaction- has the most influence on selectivity for a given ore. Thus there seems to be no straight forward solution to the selectivity problem other than a carefully designed engineering approach. The lack of effective and practical techniques to monitor and control surface reaction kinetics and the presence of so many chemical components in the flotation pulp, as well as the catalytic action of some of these components to cause certain surface reactions make even an experimental approach very challenging.

2.0 SELECTIVITY AS A MAJOR FLOTATION PARAMETER

The flotation response of an ore is traditionally assessed on the basis of grade and recovery. In a system where there is only one valuable mineral to float, a study based on grade-recovery profile is all that is required. However, in complex sulphide flotation where there is a requirement to maximize the recovery of each mineral to its respective concentrate, study based on the grade-recovery profile alone can not give sufficient knowledge of the separation process. That is why selectivity has been given a special attention in this present study.

Depending on the complexity of the ore and the state of the individual mineral components (oxidized or not) reagent combinations which may give acceptable concentrate grade and mineral recovery may be determined quite quickly. Prior knowledge of the behaviour of reagents and similar ores may help in such quick identification of chemical and physical conditions. Such empirically determined conditions, however, cannot explain how and to what extent a particular reagent contributes to overall selectivity. The degree of selectivity achieved at the early stage of flotation (during Cu- rougher flotation of a Cu/Zn ore for example) is a very important parameter but it is frequently left untested.

Unlike recovery and grade the concept of selectivity still remains poorly defined. Several selectivity indices are frequently used to define a nearly similar but not identical phenomenon flotation. Many use the term selectivity to define the difference in the rates of flotation of mineral and gangue. Others define selectivity as the difference in recoveries of the mineral to be floated and the one to be depressed to the concentrate of the other. Still others have equated selectivity to the difference in recoveries, into the concentrate of the component to be floated at a fixed recovery, of the mineral to be floated and the one to be depressed. This is to say that the selectivity of copper against zinc is indexed as the difference between the recovery of Cu and Zn into the Cu-Concentrate at a recovery of say 85% Cu.

The major difficulty in unifying the concept of selectivity seems to be the lack of an unbiased means of quantitative presentation which can give a meaningful interpretation, analogous to grade and recovery. Selectivity refers to the ability of a process (i.e. a reagent combination) to have the desired opposite effect on two minerals or two groups of minerals, that is to say depressing one or group of minerals while floating the other.

The selectivity index used in this study is defined as the ratio of the difference in recoveries (to the concentrate of the metal floated) of the metals to be separated to the recovery of the metal that is floated. Comparing the selectivity indices at a given recovery (for example 90% Cu rec.) of a metal would have been an ideal situation. However this requires determination of flotation responses covering a wide range of recoveries to exactly find the reference point (of 90% recovery).

The present definition is employed due to its relative reliability in comparing and interpreting flotation results of different operations under different conditions. For instance there is no difference in selectivity between two flotation systems which give responses of 90% Cu and 10% Zn recovery and the one which gives 45% Cu and 5% Zn recovery to the Cu concentrate. The simple subtraction of the two recoveries, which is frequently used by some investigators, would have given indices of 80 and 40 giving the erroneous impression that the first condition gives better selectivity than the second. 90% Cu and 20% Zn, 85% Cu and 15% Zn, 80% Cu and 10% Zn in copper concentrate could show the same selectivity index while in reality the reagent system which provides 80% Cu and 10% Zn is the most selective of all the systems.

3.0 LITERATURE REVIEW

3.1 THE ROOT CAUSES OF COMPLEX SULPHIDE FLOTATION SELECTIVITY PROBLEMS

The problems associated with selective flotation of complex sulphide ores are many fold and the major concern is the complexity of the flotation pulp chemistry even before the addition of reagents. The addition of different flotation reagents, the variation in levels and points of addition of these reagents and the recirculation of some of the streams further complicates the process. This makes the chemical balancing of the system practically impossible.

In particular the problems of copper/zinc flotation selectivity are caused by the presence of sulphide oxidation products such as metal oxides and secondary copper minerals. They may occur also in the form of chalcanthite ($CuSO_4.5H_2O$), free copper sulphate ions or as sulphites of copper, zinc and iron. The presence of one or the other of these compounds may prohibit the use of this or that reagent. In the presence of copper oxide minerals, for instance, the use of SO_2 as a depressant in copper/zinc selective flotation may cause a leaching of Cu^{++} which activates zinc, thereby reducing selectivity.

Sulphides are thermodynamically non-stable in the presence of oxygen. Their oxidation proceeds with a considerable intensity and speed during the stages of mining, storage and processing. It has been noted (3, 4) that the level of metal sulphates in a freshly mined Cu/Zn ore is higher than the level just before mining by many folds. Pyrite oxidizes under the action of water, oxygen, salts and other components in the pulp. The oxidation of pyrite and other sulphide minerals during grinding and flotation causes the principal problem encountered during selective flotation. With an increase in alkalinity and prolongation of grinding time, the oxygen adsorption by sulphides increases. Though the end product of sulphide oxidation is a sulphate ion, there are a few intermediate stages of chemical formation in the form of sulphoxide ions (3,23). The most stable surface oxidation products are sulphates and thiosulphates. Their formation consumes dissolved oxygen, a species greatly responsible for chemisorption of a collector, in the pulp making the pulp atmosphere too reducing inhibiting effective collector adsorption.

As the grinding time increases, the concentration of dissolved oxygen decreases and the concentrations of sulphoxy compounds increase. Sulphoxy compounds are chemisorbed by sulphides and this leads to the formation of insoluble metal sulphoxy complex salts on the surface causing a non selective depression of all sulphide minerals.

The oxidation of pyrite proceeds via its decomposition leading to formation of elemental sulphur and iron sulphide. According to Bocharov (3, 4) the amount of elemental sulphur increases with an increase in grinding time. He observed an increase in elemental sulphur from 85 mg/100 g of pyrite to 550 mg/100 g of pyrite after 80 min grinding. Though it is difficult to say with any certainty how much of the increase is due to the incr ase in particle surface area or due to the oxidation kinetics, the author has also observed that for a milling time near to that of a plant, the amount of elemental sulphur increases three times. Unless the elemental sulphur so formed is oxidized before the pulp is subjected to flotation, pyrite might prove difficult to depress. As practised by many base metal concentrating plants, both collectors and depressants may be added to the mill. The advantages and disadvantages are relative but during milling a pyritic Cu/Zn ore this practice requires thorough investigation. Research has shown that in the presence of pyrite, the oxidation of other sulphides is enhanced (11, 14, 15). The oxidation of sphalerite has been observed to increase 8 to 20 times faster in the presence of pyrite. This accelerates the formation of elemental sulphur on the surfaces of chalcopyrite and sphalerite. Sulphur formed in such a way may promote the floatability of sulphide minerals but at the same time it may cause difficulties during selective flotation. In selective flotation any uncontrolled process which promotes floatability of valuable minerals or their depression poses a potential selectivity problem.

Pyrite affects not only the oxidation of other sulphide minerals but also oxidizes xanthate to dixanthogen (20, 23) a strong sulphide collector, which may adsorb non-selectively on all sulphide minerals reducing flotation selectivity.

The quantities of sulphur formed on galena, chalcopyrite and sphalerite in the presence of iron (or during grinding in steel mill) could increase significantly when oxidation is carried out in the presence of xanthate. In the presence of iron and pyrite a significant uptake of xanthate by sphalerite was observed. These two factors - the increase in elemental sulphur and xanthate uptake by sphalerite -complement each other, rendering sphalerite floatable without activation or too difficult to depress. The practice of adding xanthate to the mill where sulphide minerals undergo surface oxidation must be examined if sphalerite tends to float without activation during the copper rougher flotation cycle. Also, the presence of some secondary copper minerals, from which copper ions are easily leached by cyanide, may increase the concentration of Cu ion thus activating sphalerite. Other heavy metal ions such as Ag, Hg, Cd and Pb, which are usually present in sulphide ores may contribute to the activation of sphalerite during the Cu flotation stage. Such inter-activation is one of the major causes of selectivity problems.

Selective flotation always calls for fine grinding and under such conditions ultrafine particles of copper and lead sulphide

minerals may be attached to sphalerite particles surfaces, leading to their flotation with copper and/or lead. Due to the differences in grindability one sulphide mineral may be preferentially ground finer than the other and the fine particles of the softer mineral may be mechanically trapped into the froth of the other mineral. As the result of this selectivity decreases.

3.2.0 PULP CHEMISTRY CONTROL TO IMPROVE SELECTIVITY OF COPPER/ZINC FLOTATION.

3.2.1 THE ROLE OF MAJOR INORGANIC DEPRESSANTS IN Cu/Zn SELECTIVE FLOTATION

ZINC SULPHATE ($ZnSO_4$)

The addition of Zn^{++} ions to the system, usually in the form of $ZnSO_4$, prevents the surface activation of sphalerite by Cu^{++} ions through an ion exchange reaction (39).

$$ZnS + Cu^{++} \longleftrightarrow CuS + Zn^{++}$$

The increase in Zn^{++} ion concentration shifts the reaction towards the left, thus inhibiting further activation. However, zinc sulphate by itself doesn't deactivate copper-activated sphalerite surfaces. In floating Cu/Zn ores containing secondary copper minerals, the effectiveness of $ZnSO_4$ is very limited and is used only as an auxiliary depressant in conjunction with cyanide.

CYANIDE

The role of cyanide in zinc depression is to dissolve any copper sulphide coating to form the soluble cupro-cyanide ion $Cu(CN)_2^-$ (38). After the dissolution of this coating the floatability of the previously copper-activated sphalerite is reduced to the normal low response of the pure mineral surface.

$$Cu^{++} + 3CN^- \longrightarrow Cu(CN)_2^- + 1/2C_2N_2^-$$

The cyanide's function is essentially that of deactivation and no significant adsorption of cyanide or copper-cyanide complex takes place on unactivated sphalerite surfaces, nor does cyanide inhibit the flotation of unactivated sphalerite (which can be floated to some extent with long chain sulphydryl collectors- amyl xanthate or amyl mercaptan).

To enhance the depression of sphalerite, cyanide and $ZnSO_4$ are used together. The de-activation by the combination of cyanide and $ZnSO_4$ is a combined result of the mass action and common ion effect of the $ZnSO_4$ in supplying zinc ions to replace copper ions on the sphalerite surface and the complexing action of cyanide on the replaced copper ions (10).

According to Gaudin, the depression mechanism of pyrite by cyanide is similar to that of sphalerite deactivation i.e. a solvent action on surface films of copper sulphide (covellite and chalcocite). However, according to Elligiani and Fuerstenau (10), the cyanide depression of pyrite is due to the formation of a hydrophilic surface ferric-ferrocyanide $Fe_4(Fe(CN)_6)$.

The concentration of cyanide ion is a function of pH, the dissociation of NaCN being nearly seventy times as great at pH 9 as it is at 7. Hence the efficiency of the added cyanide both in deactivating sphalerite and in depressing other sulphide minerals should be greater at high pH values. At high alkalinity, however, the selectivity deteriorates and a close control of cyanide, collector and alkali concentration is required. Though the major depression mechanism by CN^- ion is complexing the activating ions on the sphalerite surface and in the pulp it has been reported (29) that it also desorbs xanthate from sphalerite surface.

SULPHUR DIOXIDE (and other sulphur oxyanions)

While evidence has accumulated which supports the idea that sulphur dioxide alone or in conjunction with other modifying agents can increase the selectivity of complex sulphide flotation systems, the phenomenological reasons for this success have not been fully established. However, some possible mechanisms for the depressing effect of sulphur dioxide on sphalerite and also its use as a flotation modifier during complex sulphide ore treatment have been suggested (20):

1. Formation of hydrophobic surface deposit such as zinc sulphite or calcium sulphite (when CaO is used as a pH modifier and/or pyrite depressant).

2. Formation of insoluble heavy metal sulphite salts which reduces the heavy metal ion concentration in the pulp, thus preventing unintentional activation of sphalerite.

3. Xanthate decomposition due to a sulphur dioxide promoted oxidation reaction.

4. Limited collector adsorption due to shift in pulp potential.

In general it is believed that sulphoxy depressants (SO_2, $Na_2S_2O_3$, $NaHSO_3$, etc.) increase the concentration of free electrons on the mineral surface and decrease the adsorption of xanthate. Electrons on mineral surface react with dissolved oxygen to form hydroxide ions which is adsorbed by the mineral forming a hydrophillic surface. Increased electron concentration on mineral surface prevents the oxidation of xanthate to dixanthogen (mainly on the surfaces of chalcopyrite and galena) a strong sulphide collector which may be deposited on the surfaces of all minerals nonspecifically. Sulphur dioxide also may reduce the surface formation of elemental sulphur hence preventing self induced flotation of sulphides.

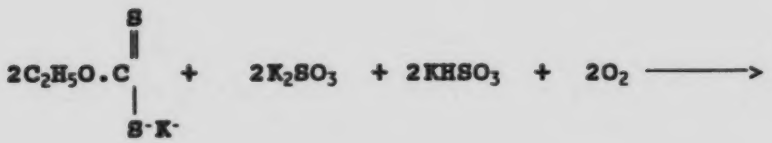
The depressing action of sulphur dioxide on various sulphide minerals in the presence of xanthate has been found to increase in the following order (20):

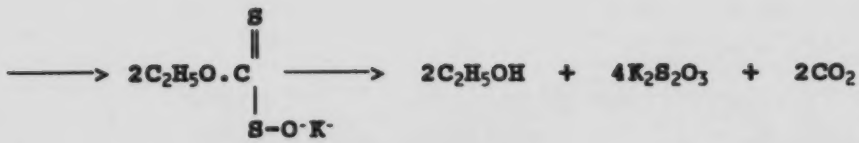
Chalcopyrite < chalcocite < covellite < galena < pyrite < marmatite < sphalerite.

Sulphur dioxide decomposes both adsorbed and excess xanthate ions in the pulp. Desorption by decomposition is however very slow under normal temperature. The decomposition of KAX in the presence of sulphur dioxide is dependent on SO_2/KAX mole ratio, dissolved oxygen concentration, and system pH. The rate of decomposition is very rapid at neutral pH (20). The rate and extent of amyl xanthate adsorption by chalcopyrite was found to be at least an order of magnitude greater than the adsorption by sphalerite. Depression of sphalerite occurs when the SO_2 solution molar concentration is fifty times greater than the xanthate concentration or when an extended decomposition time is allowed at lower SO_2 concentration. Misira et. al. (20) suggest that dissolved SO_2 is required to decompose amyl xanthate and consequently prevent the flotation of sphalerite during selective flotation of chalcopyrite. According to these investigators, in a complex mineral flotation system, the adsorption of xanthate on chalcopyrite is much faster than its decomposition by SO_2. Therefore chalcopyrite may be selectively floated from sphalerite and pyrite when SO_2 is used as a depressant (or regulator).

The decomposition mechanism of xanthate by sulphite ion and oxygen has been investigated by Yamamoto (29). The decomposition products were determined by ultraviolet absorption spectroscopy and by Raman Spectroscopy.

The decomposition mechanism proposed is:





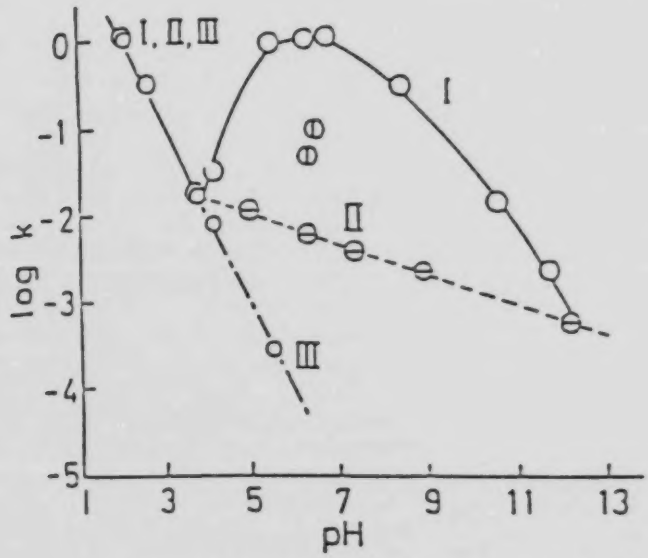
After xanthate is decomposed,sulphate ions are formed from oxidation of bisulphite and the pH value of the solution is lowered.

Flotation test results for pyrite and activated sphalerite from this study are shown in fig. 3.1.

The similarity of the range of pH values between complete depression in pyrite flotation and rapid decomposition of xanthate by sulphite and oxygen (curve I) suggests that pyrite depression by sulphite is due to pyrite surface desorption and free xanthate decomposition. The action of sulphite in desorbing xanthate from Cu-activated sphalerite is, however, limited.

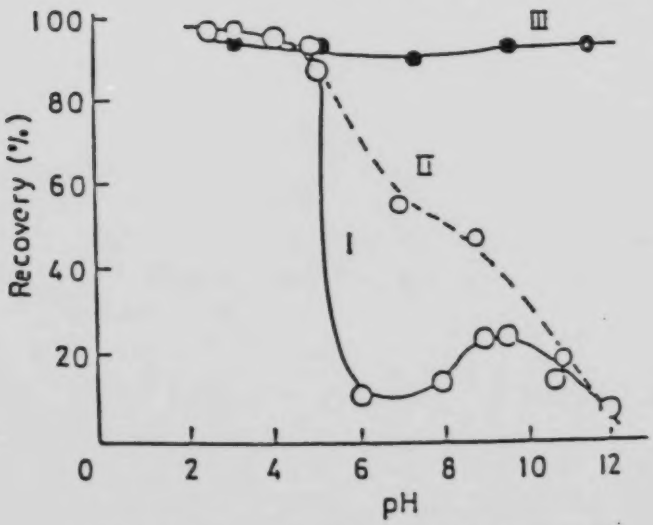
Surface cleaning of chalcopyrite due to the action of SO_2 and chalcopyrite surface has also been observed. According to Misra, when chalcopyrite was treated with SO_2 solution and the SO_2 subsequently removed by careful decantation, an enhanced flotation recovery with KAX was observed. The result of this study is presented in table 3.1. As may be seen from this table pretreatment of chalcopyrite with SO_2 for 5 min., decanting and reconditioning it in distilled water induced collectorless floatability, as observed by an increase in recovery from 5% to 59%.

Figure 3.1A. Relationship between pH and decomposition rates(k) of xanthate by sulphate.



Relationship between pH and decomposition rates (k) of xanthate by sulphite: I. ○ oxygen, ⊖ nitrogen; II. ⊖ on standing; III. decomposition of xanthic acid

Figure 3.1B. Effect of sulphite on flotation recovery of pyritic or copper activated sphalerite at different pH.



Effect of sulphite on flotation recovery of pyrite or copper-activated sphalerite at different pH: I. flotation recovery of +400 −200 mesh pyrite with 1×10^{-4} M xanthate and 4×10^{-2} M sodium sulphite; II. flotation recovery of pyrite with 1×10^{-4} M xanthate; III. flotation recovery of +400 −200 mesh copper-activated sphalerite with 4×10^{-4} M xanthate and 4×10^{-2} M sodium sulphite

Table 3.1. Effect of SO_2 pretreatment (cleaning) on chalcopyrite flotation with amyl xanthate (after SO_2 removal, pH 6.5) (20).

SO_2,Conc., M	KAX, conc., M	Recovery,%
None	None	5.00
None	1.08×10^{-4}	74.77
2.5×10^{-2}	None	59.77
2.5×10^{-2}	1.08×10^{-4}	100.00

The following conditions all enhance the selectivity of chalcopyrite against sphalerite (and also pyrite):

- the cleaning action of SO_2 (of chalcopyrite surface) and its ability to control sulphide surface potential;
- the higher rate of adsorption of xanthate on chalcopyrite surface compared to its rate of decomposition by SO_2;
- the lower adsorption rate of amyl xanthate on sphalerite by an order of magnitude,

CHEMISTRY OF SULPHUR DIOXIDE

Though SO_2 when dissolved in water can be written as "H_2SO_3" the action of sulphurous acid, even if not completely different, is reported by many not to be exactly the same as that of sulphur dioxide. In the present literature survey, however, it has been observed that whenever and wherever the two compounds were used alone or in combination with other depressants, the flotation selectivity improved. Note that "H_2SO_3" the water solution of SO_2 does not exist as a species and dissociates into hydrogen ion and hydrogen sulphite (23).

$$\text{"}H_2SO_3\text{"} \longrightarrow H^+ + HSO_3^{2-}$$

$$HSO_3^{2-} \longrightarrow H^+ + SO_3^{2-}$$

H_2SO_3 - may decompose according to the reaction :

$$2HSO_3 \longrightarrow S_2O_5^{2-} + H_2O$$

From the oxidation state of the sulphur atom in these equations it is possible to see that both sulphite and hydrogen sulphite ions are reducing agents. Sulphite ion is an excellent complexing agent and most metal sulphites with the exception of alkali and ammonium, are insoluble. This may describe its effect as a depressant.

The reduction behaviour of an aqueous sulphur dioxide solution may be written as a redox reaction (23):

$$SO_3^{2-} + 2OH^- \longrightarrow SO_4^{2-} + H_2O + 2e^-$$

$$E^0 = 0.43\ V$$

sulphurous acid can also act as an oxidizing agent to produce thiosulphate according to the reaction:

$$" H_2SO_3" + S \longrightarrow H_2S_2O_3$$

3.3. PLANT EXPERIENCES

On replacing $ZnSO_4$ by SO_2 as a major Zn depressant in the Cu flotation circuit of the Stekenjokk concentrator (6) at a pH of 10.5 (adjusted by lime) a considerable reduction of Zn in Cu concentrate was achieved- from an average of about 10% (over a 6 year period) to an average of 6% (over a 2 year period) as may be observed from the graph in fig. 3.2.

In another copper/lead flotation circuit at the Garpenberg concentrator in Sweden, SO_2 improved the overall metallurgy. Two test results on an ore which was reported to be particularly difficult to dress are presented in table 3.2 A and B to demonstrate the tremendous improvement as the result of replacing zinc sulphate, cyanide, and sodium sulphide by SO_2 as a major zinc depressant. However, it was reported that SO_2, dithiophosphate and starch improved the plant metallurgy even further. The operating plant metallurgical result is also presented for comparison in table 3.3 A and B. SO_2 addition reduced zinc grade in the copper/lead bulk concentrate and helped to increase the copper yield though lead loss to the tailings increased slightly. This is in conformity with other results noted herein, that SO_2 "activates" chalcopyrite and depresses sphalerite.

Bulatovic, et. al (7) noted that SO_2, when used with lime improved the selectivity of a refractive complex sulphide ore, but the effect of the addition points of lime and H_2SO_3 was found to

the effect of the addition points of lime and H_2SO_3 was found to be the most important parameter. Excellent Cu/Zn separation was achieved when H_2SO_3 was added to the mill and lime to the conditioner while the addition of lime to the mill had a negative effect on zinc recovery. This was thought to be due to the effect of lime in encouraging the activation of sphalerite due to greater solubility of chalcopyrite oxidation products at higher pH values.

Figure 3.2 (6). The Stekenjokk Concentrator. Zn-grade in copper concentrate for the period 1976-1983.

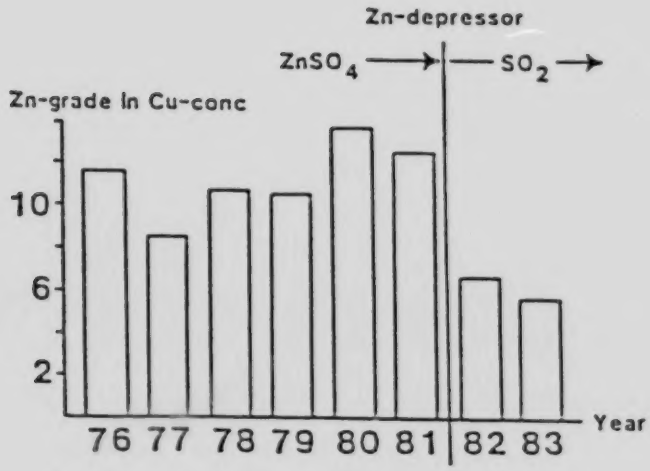


Table 3.2. Effect of $ZnSO_4$ replacement by SO_2 on Cu/selectivity; Lab test (6).

A. Nat pH = 11, zinc sulphate, cyanide, starch, Na_2S, xanthate									
Products	weight	Assay				Recovery			
	%	Ag g/t	Cu %	Pb %	Zn %	Ag %	Cu %	Pb %	Zn %
Cu/Pb rougher con.	14	496	1.0	18.9	15.4	73	49	61	41
Cu/PB tailing	86	30	0.17	2.0	3.7	27	51	39	59
Feed	100	96	0.29	4.4	5.4	100	100	100	100
B. SO_2 pH = 7.2, starch, xanthate.									
Products	weight	Assay				Recovery			
	%	Ag g/t	Cu %	Pb %	Zn %	Ag %	Cu %	Pb %	Zn %
Cu/Pb rougher con.	13	607	1.9	20.7	8.2	82	85	62	20
Cu/PB tailing	87	20	0.05	1.9	5.1	18	15	38	80
Feed	100	98	0.30	4.4	5.5	100	100	100	100

Table 3.3. Effect of $ZnSO_4$ replacement by SO_2 on Cu/selectivity at the Garpenberg Concentrator (6).

A. 18 month production prior to the introduction of SO_2.											
Product	Weight	Assay					Recovery				
	ton	Au g/t	Ag g/t	Cu %	Pb %	Zn %	Au %	Ag %	Cu %	Pb %	Zn %
Cu conc	4,770	33.1	1901	13.50	12.20	22.6	59.9	29.0	62.0	5.7	7.4
Pb conc	12,268	2.8	936	0.72	60.60	10.2	13.1	36.8	8.4	72.4	8.7
Zn conc	20,664	1.1	165	0.63	2.31	53.2	8.2	10.9	12.5	4.7	76.0
Tailing	232,801	0.2	31	0.08	0.76	0.5	18.8	23.3	17.1	17.2	7.9
Feed	270,503	1.0	116	0.39	3.80	5.4	100	100	100	100	100
B. 18 months production after the introduction of SO_2.											
Product	Weight	Assay					Recovery				
	ton	Au g/t	Ag g/t	Cu %	Pb %	Zn %	Au %	Ag %	Cu %	Pb %	Zn %
Cu conc	3,970	48.2	2003	19.80	11.80	10.70	68.3	30.6	78.7	4.9	3.1
Pb conc	11,078	2.8	931	0.67	58.50	9.24	11.3	40.2	7.4	67.3	7.4
Zn conc	25,510	0.6	109	0.28	2.78	53.70	4.4	8.6	5.8	5.9	79.4
Tailing	228,134	0.2	24	0.04	0.92	0.61	16.0	21.0	8.1	21.9	10.1
Feed	263,692	0.1	98	0.38	3.65	5.25	100	100	100	100	100

Feed: tailing from the talc flotation circuit.

The effect of sulphur dioxide on Cu/Zn flotation selectivity can be observed from tables 3.2, 3.3 and 3.4, in which the selectivity index is calculated as a ratio of the difference between the recoveries of metal A and metal B into the concentrate of A to the recovery of A. Thus if the recovery of Cu into the Cu-concentrate is a% and the recovery of Zn into the same concentrate is b%, then the selectivity of Cu separation from Zn is defined as:

$$(SI)_{Cu/Zn} = (a - b) / a$$

Table 3.4 is derived from table 3.3 in order to compare the effects of SO_2 and $ZnSO_4$ on Cu/Pb/Zn flotation selectivity. For the Zn-circuit the selectivity of Zn flotation with respect to Cu or to other minerals is based on the grade of the feed to the circuit and not based on the mill head grade.

Table 3.4. Selectivity indices calculated from table 3.3.

DEPRESS	ROUGH./SCAV. FLOT. STAGE		Cu/Pb FLOT. STAGE		Zn FLOT. STAGE	
	(Cu + Pb)/Zn	Cu/Zn	Pb/Zn	Cu/Pb	Zn/Cu	Zn/Pb
$ZnSO_4$	0.792	0.769	0.914	0.917	0.545	0.76
SO_2	0.857	0.877	0.855	0.926	0.976	0.45

The improvement in selectivity as a result of introducing sulphur dioxide of Cu and Pb against Zn during Cu/Pb bulk flotation, and Cu against Pb during the subsequent separation of Pb from Cu is evident from table 3.4. This was accompanied by an increase in recovery of Cu and Zn to their respective concentrates by 27% and 4.5% respectively, while the recovery of Pb decreased by 7%. Moreover the Cu concentrate grade increased from 13.5 to 19.8%.

As may be seen from table 3.4, in the Zn circuit, Zn flotation selectivity against Pb has decreased significantly; this indicates that collector desorption from the galena surface is probably slower than desorption from chalcopyrite which was almost totally depressed at a very high recovery of Zn. More examples where the sulphite ion shows superior results in imparting selectivity to the complex sulphide minerals flotation system are given in tables 3.5 and 3.6.

3.4. LABORATORY AND PILOT PLANT EXPERIENCES

In table 3.6, in run No. 2, 3 and 4, where SO_2 was used in conjunction with Na_2S the flotation selectivity OF COPPER against zinc is higher than when a zinc sulphate and cyanide combination was used along with lime. In the case of No.1 and 2, not only the selectivity increased but also the grades and the recoveries of both metals. In No. 5 and 6 sulphur dioxide when used in conjunction with the organic depressant DS22 or cyanide it enhanced the selectivity of the minerals against each other to a greater degree. However, when used alone it does not seem to be very efficient.

In all these comparisons we are dealing with different ores treated under different conditions and the conclusions should be regarded with caution. Nevertheless, it can be seen that a general trend exists and it shows that the use of sulphite ion in conjunction with other major depressants of zinc and iron gives better selectivity. In table 3.5 in No. 1, 2 and 3, the sulphite ion is absent and the selectivity was poorer, especially in the case of No, 2 and 3.

Table 3.5. Enhancement of selectivity by SO_2 (7).

No.	Depressant	SI	Ore type	remark
1	CaO, $ZnSO_4$,NaCN	0.895	Complex Cu/Zn with some second. Cu-min.	
2	Na_2S, SO_2	0.961	"	
3	Na_2S, SO_2	0.959	Massive refractory Cu/Zn	Laborat.
	Na_2S, SO_2	0.976	"	Pilot pl
5	CaO, DS22, SO_2	0.816		
	CaO, SO_2	0.615		
6	CaO, CN.	0.770		
	CaO, CN., SO_2	0.913		

Table 3.6. Effect of various depressant combinations on Cu/Zn selectivity.

Depressant combinations	SI	Source(ref.)
1. CaO, NaCN, $ZnSO_4.7H_2O$)	0.791	de Kok
2. Na_2S, $ZnSO_4$	0.688	Shubov
3. NaCN, $Ca(OH)_2$	0.564	Uzun
4. $Ca(OH)_2$, SO_2	0.813	"
5. Na_2S, $ZnSO_4$, Na_2SO_3	0.783	Sulina
6. Na_2S, $ZnSO_4$, Na_2SO_3	0.791	"
7. Na_2S, $ZnSO_4$, Na_2SO_3	0.833	"
8. Na_2S, $ZnSO_4$, Na_2SO_3	0.944	"

Note: No. 3 and 4 are the same ore.

On the basis of the foregoing analysis of Cu/Zn separation data from different operating plants and laboratory tests, the following general conclusions can be made regarding the role of SO_2 ion in complex sulphide flotation:

1. when used as a zinc and pyrite depressant in conjunction with other known depressants (CN^-, HS^-, $ZnSO_4$, or organic depressants), it improves selectivity, grade and recovery.

2. Sulphur dioxide alone cannot produce effective depression of zinc and iron.

3. Despite the fact that some investigators (17) believe that sulphur dioxide cannot be used for an ore with secondary Cu-minerals (even at concentrations of such minerals as low as 0.1%) with a proper balance of zinc, cyanide, and sulphite ion concentrations, the Zn activation by leached Cu ions may be suppressed allowing the separation of the minerals at an acceptable level of selectivity.

4. Selectivity is improved when sulphur dioxide is used in conjunction with one or two other depressants.

3.5 THE ROLE OF GRINDING MEDIA IN SELECTIVE FLOTATION OF COMPLEX SULPHIDE MINERALS

Grinding media has been recognized to have an effect on the flotation response of complex sulphide ores and, in particular on their selective separation. Results of various investigations show that, although its effect depends on its composition, iron acts quite differently from the other types of grinding media, for example such as ceramic or pebbles. This difference may be explained by the galvanic interaction between metallic iron and the semi-conducting sulphide minerals (22). Sulphide minerals are semi-conductors and they assume different potentials in different aqueous media. If they make contact with each other or with other conducting surfaces an analog to electrochemical (galvanic) cell will form. The mineral or conductor with the highest rest potential will act as a cathode electrode while the anode will be the mineral or material with the lower rest potential.

A study of the effect of grinding media on the selectivity of copper/zinc ore (5)revealed that:

1. Increased sphalerite liberation was obtained when the grinding media was either flint-ceramic pebbles or ore fragments (autogenous grinding) instead of steel balls. Consequently, flotation responses indicated an improvement in copper and zinc recovery. The analysis of the results indicates that the increase in recovery of zinc can be accounted for by the increased degree of mineral liberation; however, the disproportionate increase in copper recovery in going from steel to pebbles (from 78% to 82%) is not possible to explain fully by the slight increase in liberation (4.8%), because the recovery of free chalcopyrite into the concentrate increased by 14.5%. This indicates that factors other than particle liberation were also active. An explanation of this effect will be presented later.

2. The copper concentrate grade dropped in going from steel to pebble to autogenous, while zinc in copper concentrate increased in going from steel to pebble to autogenous grinding. It was also observed that fewer free sphalerite particles reported to the copper concentrate when the ore was ground in a steel ball mill than in either a pebble or autogenous mill. This is in conformity with earlier results which showed that sphalerite is more depressed during copper flotation when the ore is ground in the presence of steel than in its absence. Even though the figures are very close to each other, they are averages of four to five continuous pilot tests each conducted over a time interval of about twelve hours, and the conclusions may be considered reliable.

In changing from ordinary rod and ball mill grinding to autogenous grinding at Boliden-Sweden (16) sphalerite became

Bushell and Veitch (16) found that the type of mill and the chemical environment in the mill, as well as the source of the ore had a profound effect on the hydrophobicity of sphalerite. In their experiment they produced a copper or copper/lead concentrate after grinding in the presence of zinc sulphate as a depressant for sphalerite. The tailings of these flotation tests were then activated by copper sulphate and then the sphalerite floated. Xanthate collectors were employed. Due to its relevance to the present study the table of results of their test is presented in table 3.7.

In their experiment the copper and lead recoveries did not change in any of the tests and the zinc content of the tailings remained the same. Therefore, it was assumed that the reduced recoveries were caused by activated or naturally floating sphalerite floating with the copper or copper/lead concentrate. Their test was designed to reduce sphalerite activity by changing the chemical environment during the grinding of the ore (G759)

Table 3.7. Grinding media effect on sphalerite flotation (16).

Z I N C R E C O V E R Y (%)					
SAMPLE	ORE TYPE	MILD STEEL MILL & RODS	MILD STEEL MILL & BALLS	STAINLESS STEEL MILL & BALLS	PROCEL. MILL
G759	Cu/Pb/Zn	56	55	20	3
G511	Cu/Pb/Zn	64	-	58	36
G758	Cu/Pb/Zn	49	-	14	5
G815	Cu/Zn	59	-	26	3
G816	Cu/Zn	81	-	78	78
		MILD STEEL SHELL & ORE PEBBLES	STAINLESS STEEL SHELL & ORE PEBBLE	PORCELAIN SHELL & ORE PEBBLES	PORCEL. SHELL & STEEL B.
G759	Cu/Zn/Pb	50	17	11	51
G759	Cu/Zn	68	17	14	

independently of the material of construction of the mill by using a porcelain mill with porcelain balls, indicated that an addition of NaCN (0.3 g/kg of ore) and iron powder gave the highest recovery of Zn into Zn-concentrate.

Then the effect of iron powder, zinc sulphate, and sodium cyanide and their combinations were tested. When the same sample (G759) was tested, after grinding it in a mild steel rod mill

(table 3.7), with the combination that gave the best selectivity after grinding in a porcelain mill with porcelain balls, (table 3.7), the results showed that neither iron powder nor zinc sulphate as depressants improved selectivity. However, the addition of iron powder (30 g per kg of ore) to the mill restored the sphalerite recovery to the high value obtained when using the mild steel mill (68%). Only NaCN (up to 500 ppm), increased the sphalerite recovery (to 70%) without affecting the copper recovery.

From these two independent studies it is possible to make one common conclusion that zinc is more efficiently depressed when the complex ore is ground in a mild steel mill in the presence of NaCN, and for every ore type there exists an optimum cyanide quantity. Iron, in the form of either shell liners or grinding media (balls, rods) or both, has an effective depressing effect upon sphalerite. When the amount of the commonly used depressants such as NaCN and $ZnSO_4$ exceeds an optimum value, an irreversible Zn and/or Cu/Pb depression may occur, while at a low level they may not depress sphalerite efficiently. Iron or steel mills seem to help overcome this particular problem and such milling equipment seems to be essential for the selective recovery of zinc from nearly all complex sulphide ores.

3.6 PULP POTENTIAL AS A PROCESS CONTROL PARAMETER

Many researchers have recognized the dependence of complex sulphide flotation selectivity on the pulp electrochemical potential. Several notations have been used by different investigators and the lack of standard measurement procedure has lead to some confusion. Eh, rest potential, reversible potential and standard potential all imply that the system was at equilibrium when the measurement was made. They all have a more precise meanings (43). Eh implies that the potential measured or calculated is referenced to the Standard Hydrogen Electrode (SHE). The electrochemical potential (E) and oxidation-reduction (redox) potential are general terms. They do not imply any particular condition for the system being studied except that a measurement was taken. Solution, mixed, galvanic, and pulp potential are the other group of potential measurements. These are measurements taken under dynamic conditions. Mixed potential is a generic term for a potential measured in a complex system such as the flotation pulp. The potential reading we get by dipping an electrode in a stirred pulp is a function of many parameters and is, in fact, a mixed potential (34, 36). Solution potential deals with only ions in the pulp solution and the galvanic potential looks only at the solids, in contact. Physical contact need not be necessary for a galvanic contact to occur between two solids. The ions in the solution may "transport" the electrons from one solid to the other by entering oxidation/ reduction reactions at the solid surfaces (43). The pulp potential, E_p, and E_{pt}, have been used to describe the potential

measured in a mineral slurry. This potential is neither equal to the solution potential nor to the galvanic potential of the minerals, but takes a value which is the result of the net effect of the two on the slurry.

The selectivity of sulphide minerals flotation is believed to be closely associated with the differential potentials developed on the surfaces of mineral particles. The possibility of using pulp potential to control grinding and pulp pretreatment conditions has been the object of many investigations. In the last 20 years a considerable amount of research has been done to understand the electrochemistry of complex sulphide flotation pulps. However, there has been no method developed for quantitative evaluation of individual redox reactions that occur during pulp conditioning. Instead a qualitative evaluation of the overall electrochemical change by measuring the so called "pulp redox potential" has been tried. This potential has been frequently referred to as Eh by many investigators and it has been correlated to flotation responses. The precise meaning of Eh in a complex sulphide pulp, however remains obscure (31, 34).

The potential developed in a flotation pulp is a function of the total surface area of sulphide particles, pH, and the presence and levels of modifiers, frothers and collectors (30, 34, 36). Unless all these conditions are determined the potential reading we get is not meaningful (34).

In spite of the difficulties associated with understanding the precise redox reactions that take place in complex sulphide flotation pulp, pulp potential has a potential of being used as a convenient unit of measure of pulp conditions. It has been shown to be particularly important in controlling certain conditions and thus flotation responses. The development of this control technique has been very slow due to the sensitivity of the measurement to the actual flow of reagent introduced, for example, to the conditioner giving rise to extremely noisy measurements (43). Hence the selection of the point of measurement is very critical.

Natarajan and Iwasaki (22) have investigated the practical implications of pulp potential measurements in sulphide flotation circuits. They observed a close relationship between the potential readings, over a certain range, in a differential flotation circuit conditioners and the floatability of sulphides and the selectivity between them. They also concluded that the poisoning of platinum electrode with sulphide species in alkaline pH regions is minimal and by frequent cleaning of the electrodes, oxygen levels in the pulp may be monitored and related to the flotation behaviour of the sulphide ores.

The dependence of the flotation response of several sulphide minerals, such as pyrite, chalcopyrite, bornite, and chalcocite, on electrochemical potential was established by the US Bureau of Mines(35). Johnson and co-workers (31) conducted a pulp Eh survey

in a Pb-Zn-Fe sulphide separation plant at Mount Isa (Australia), performed bench tests and proved the hypothesis that the low potential reading arises from the strongly reducing environment in grinding circuits that leads to galena depression. They also observed an occasional variation in potential readings, the values falling mostly between +110 mV and +130 mV. Their laboratory test results also indicate that the initial pulp potential had a major influence on the results.

The use of potential variation to control differential flotation was investigated also by Gebhardt and Richardson (35). They observed that the flotation behaviour of chalcocite and pyrite within the same range of potential is different than the behaviour of individual minerals indicating that the presence of one mineral affects the behaviour of the other. They clearly indicated that there exists a correlation between the potential reading and the flotation response and that control of the electrochemical potential is a viable way to selectively float complex sulphide ores.

Beyzavi and Kitschen (30) conducted an investigation on three different Cu/Pb/Zn pyritic ores and observed that an optimum adjustment of the pulp potential prior to the first flotation stage, particularly the copper flotation stage, considerably improves the selectivity. They also suggested that the flotation kinetics can be improved by measuring and controlling the pulp potential.

In his study on the role of sodium sulphide in the flotation of oxidized Cu/Pb/Zn ores, Malghan (37) used two types of potential measurements- platinum and sulphide specific electrode against a saturated calomel electrode. Obviously the two electrodes measured different quantities. Nevertheless they observed that the measured value E_s was consistently half of the potential value E_{pt} over a flotation period of 30 minutes. (The potential value E_{pt} was the mixed potential and E_s was the level of S^{2-} in the pulp). Due to this direct correlation between the two readings they commented that the platinum electrode could be used as well for indicating sulphide ion concentration and even recommended the use of a platinum electrode under such cases because it is robust and trouble-free. When they used a potential controlled dosage of sodium sulphide they achieved a much higher Pb concentrate grade and Pb/Zn selectivity compared to slug addition. Similar correlation between E_{pt} and O_2 concentration in a complex sulphide flotation pulp has also been reported (30).

Based on the results of these investigations, it can be concluded that a pulp potential measurement could be used as a selectivity control parameter. The measured values apply only to that particular ore and set of reagent conditions, pulp density, agitation speed, pH and grind size (specific surface area) and they may change if any of these operating parameters change. The magnitude of this change and the sensitivity of flotation responses

to such a change determine whether pulp potential measurement could be successfully used or not.

3.7 NON-CHEMICAL TECHNIQUES OF IMPROVING SULPHIDE MINERALS FLOTATION SELECTIVITY.

Selectivity may be improved by manipulating process routes to include certain appropriate unit operations (such as an intermediate classification). Different particle sizes of the same mineral have different flotation as well as depression characteristics. Floatabilities of particles of the same mineral may be affected by other parameters such as shape, surface configuration, cleavage geometry and the presence of active sites on the surface.

Pulling harder to improve the recovery of less floatable minerals through an increase in collector will cause Zn, which is otherwise depressed, to float. Likewise, depressing the highly floatable Zn by using a higher dosage of depressants may cause complete depression of low floatability Cu and Zn. Separate treatment of components (of different minerals) of similar floatability (equal kinetics) may solve such common problems. As an example, let us consider the results in table 3.8 (9), where an addition of 10 g/t NaCN gave 93.9% Cu and 51.8% Zn recoveries into Cu-conc. We can thus have two components: a highly floatable component to which 94% of total Cu and 52% of total Zn, reported and the other which contains about 6% of total Cu and 48% of total Zn. The second component is a high Zn low Cu fraction and may be treated in an independent circuit and with a little more collector it would be possible to recover some of the depressed copper. Since 6% of total Cu is a normally acceptable loss the second fraction can also be treated only for its contained zinc. If a combination of $ZnSO_4$ and NaCN at a level of only 350 g/t and 20 g/t respectively, calculated on the basis of feed, is used to depress Zn in the first fraction the depression may be effective without affecting Cu-recovery.

This concept of selective separation based on separate treatment of equally floatable minerals has found a practical application in China for processing complex, low-grade and fine grained sulphide ores. A conventional flowsheet and the flowsheet developed based on the concept of separate treatment of particles of "equal floatability" for the selective flotation of Mo and Cu is presented in figure 3.4 (13). The metallurgical results of the two flowsheets is compared in table 3.9.

Table 3.8. Effect of $ZnSO_4$ and NaCN on Cu/Zn selectivity (9)

$ZnSO_4$ g/t	NaCN g/t	%Cu in Cu con	% Zn in Cu con	Cu rec %	Zn rec to Cu con %	SI
0	0	9.48	8.58	91.8	64.5	0.2974
100	0	8.84	7.33	87.7	52.1	0.4059
300	0	8.55	6.92	83.5	49.8	0.4035
700	0	8.22	6.34	78.9	43.3	0.4512
1000	0	8.65	6.48	89.0	46.9	0.4730
5000	0	7.67	5.25	62.7	30.2	0.5183
0	10	12.55	8.88	93.9	51.8	0.4483
100	10	11.30	8.34	84.5	50.8	0.3988
300	10	15.76	6.58	88.5	28.1	0.6825
0	20	12.30	10.09	93.6	59.0	0.3697
100	20	14.78	7.88	88.0	37.3	0.5830
300	20	14.94	6.74	89.9	31.1	0.6541
0	50	13.84	5.58	50.4	15.4	0.6944
100	50	15.65	6.46	90.4	29.5	0.6737
300	50	16.07	5.77	83.3	23.2	0.7215
700	50	21.47	3.35	77.5	9.8	0.8735
1000	50	21.70	3.24	76.3	10.8	0.8585
0	100	10.01	5.49	29.3	12.2	0.5836
100	100	17.53	5.21	81.3	19.5	0.7601
300	100	17.20	5.03	80.3	17.5	0.7821
700	100	10.41	3.65	17.4	4.9	0.7184
1000	100	8.98	3.73	20.9	7.1	0.6603
0	200	5.93	4.02	14.4	7.5	0.4792
700	200	7.27	4.02	17.3	6.4	0.6301

Collectors MINEREC 1331 (13 g/t)
MINEREC 27 (27 g/t)
Frother: Dowfroth 250

Figure 3.3. A response surface constructed from table 3.8

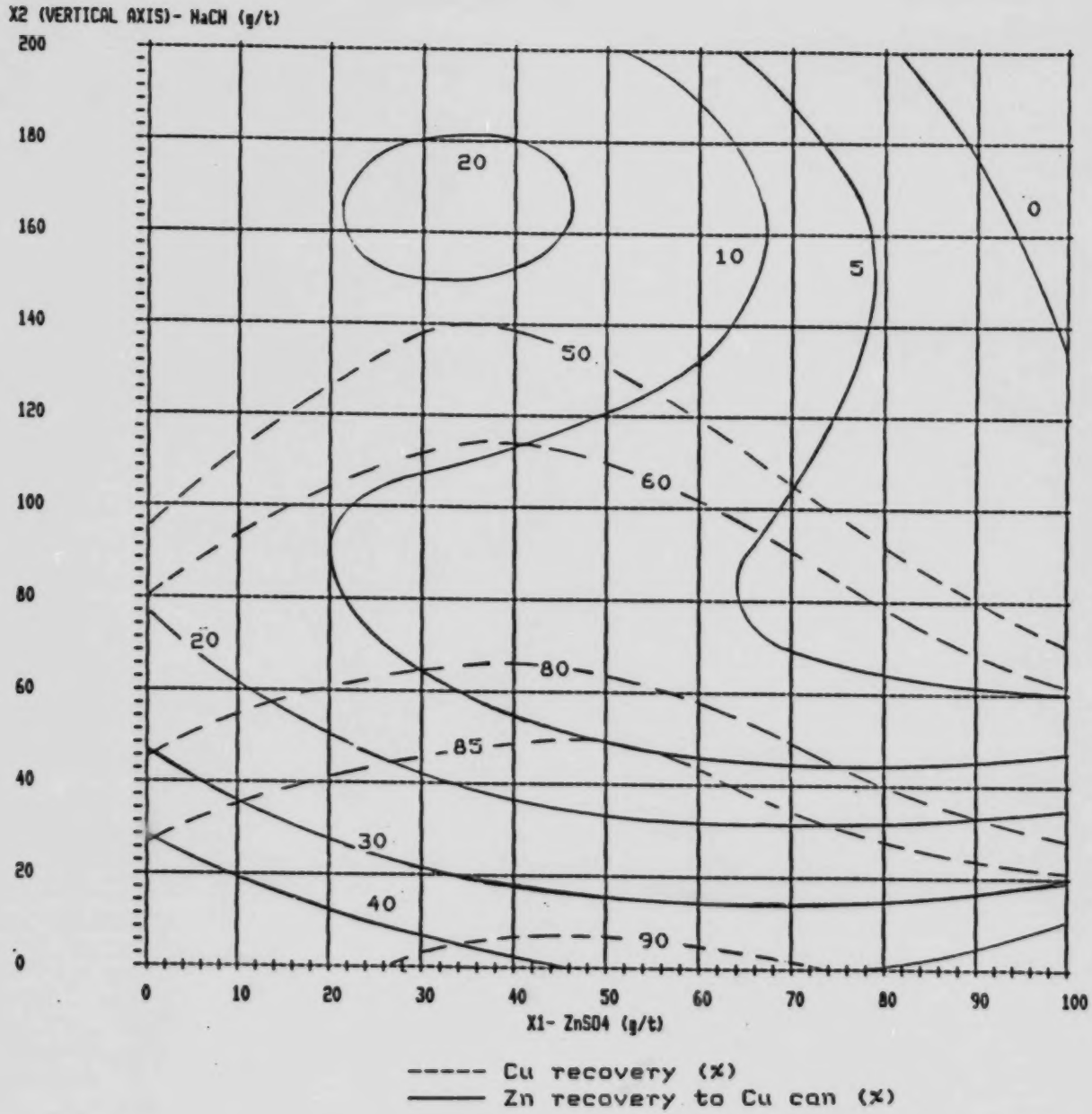


Figure 3.4. (13)

(A) A conventional flotation scheme

(B) Flotation based on the principle of separate treatment of minerals of equal floatability

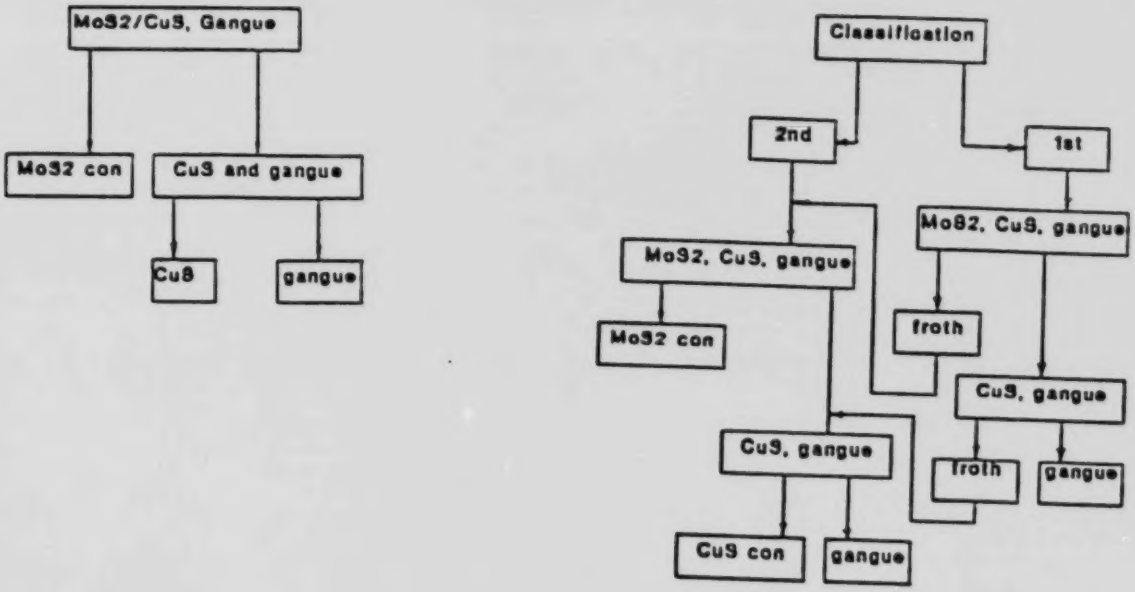


Table 3.9. Comparison of a conventional flowsheet and a flowsheet developed based on separate treatment of minerals of similar floatability (13)

	A					B				
	con. grade %		recov. %		SI	con. grade %		recov. %		SI
	Mo	Cu	Mo	Cu		Mo	Cu	Mo	Cu	
Mo RGHR con	0.23	0.51	85.6	10.3	0.88	0.60	0.52	87.0	5.0	0.93
Cu RGHR con	0.08	3.48	3.5	85.1	0.96	0.07	7.20	1.4	91.5	0.98
Tailing	0.002	0.01	10.9	4.6	-	0.003	0.01	11.6	2.7	-

The results in table 3.9 indicate the superior performance of the new flowsheet. The Mo rougher concentrate grade tripled while that of Cu doubled. The recovery of each metal to its respective concentrate increased significantly as may be observed from the increase in selectivity index in both the circuits. Hence independent treatment of components of similar floatability allows more selective depression (selective flotation) of minerals and the overall recovery of the metals to their respective concentrates is accordingly higher than when the components are all treated in the same circuit and reagent concentrations.

4.0 TEST WORK PROCEDURES, METHODOLOGY AND RESULTS

The investigation of optimum conditions for selective depression of zinc in order to selectively float Cu is the major objective of this study. The idea is to identify conditions which provide maximum differential depression of sphalerite against chalcopyrite at the early stage of flotation. This requires a more careful treatment of the pulp during grinding and conditioning. After identifying such conditions of maximum differential depression were identified then a step towards determining conditions other than reagents that affect the recovery of chalcopyrite were investigated. This unique strategy is a result of considerations of different electrochemical conditions that result during grinding in a steel mill and the addition of depressants during grinding.

4.1 TEST PROCEDURE

An ore sample from the Trout Lake deposit of the Hudson Bay Mines and Smelting Company, was used for this study. This sample was taken from the rod mill feed of the flotation circuit and was received as -1". Since the selectivity of the flotation process is a function of many interactive parameters, and there is no easy way of identifying the most influential ones, a statistical approach was selected to screen them. For this purpose an available experimental design package based on the Plackett & Burman methodology was used. HBMS's experience with the ore indicated that depressing sphalerite in the copper rougher flotation stage was very difficult; this was confirmed by recent work at CANMET (9). Yet a detailed mineralogical study (32) indicates that there is no significant liberation problem at the grinding size of d_{60} = 45 microns.

After the result of this recent study (9) was analyzed (see table 3.8 and fig. 3.3) it became evident that using Zn^{++} and CN^{-} ions alone no acceptable selectivity could be achieved. As may be observed in fig. 3.3 with this reagent system the minimum possible Zn recovery to Cu concentrate at 85% Cu recovery is unacceptably high ie. 20%. In view of this, fourteen factors were chosen to be screened. These factors are:

(a) **Reagents**

depressants:	1. $ZnSO_4$	2. KCN	3. CaO	4. SO_2
collectors	1. Potassium amyl xanthate for chalcopyrite			
	2. Sodium Ethyl Xanthate for sphalerite			
frother:	MIBC for both chalcopyrite and sphalerite.			
activator	$CuSO_4$ for sphalerite			

(b) **Conditions**

1. Aeration time
2. Cu flotation pH
3. Zn flotation pH
4. Cu flotation time
5. Zn flotation time

The Plackett & Burman factorial design was used for parameter screening. This experimental design technique has two major advantages. Many factors can be studied with a small number of tests and during analysis of the results it indicates the effect of any other factor not included in the design but has a significant effect on the response. The challenge is then finding what this factor is in order to control it or to include it in the subsequent design. The major disadvantage of this design technique is that the effects of the factors are often superimposed and are thus confused. However, a prior knowledge of the qualitative effect of each of the parameters and their possible interactions can help in arranging them in such a way that the confusion can be partly eliminated.

GRINDING CONDITIONS

The depressants were weighed and added to the rod mill and a batch grinding procedure was followed. Nine minutes grinding was sufficient to give the desired feed size of d_{80} = 75 microns.

Rod mill charge:

weight of rods	17.5 kg
weight of sample	0.9 kg
pulp density	66% solid
temperature	19 - 21 ^0C

FLOTATION CONDITIONS

Flotation was carried out in a three litre Denver pyrex glass cell under a controlled air flow rate at a pressure of 2 kg/cm^2.

pulp density	32% solid
agitation speed	13500 rpm
air flow rate	3.5 l/min

The mill discharge was transferred to the cell immediately and the equilibrium pulp pH was noted after 3 minutes agitation. Zinc activation was carried out at the pH value at which the copper flotation terminated but the pH was raised to its flotation value before the collector and the frother were added. Also the pH value for copper flotation was adjusted before the collector and frother were added. In each case the pulp was conditioned for three minutes after the collector and frother were added and the pH value was not allowed to fluctuate more than 0.05 units both during conditioning and flotation. The pH values were adjusted using sulphuric acid and lime.

4.2. RESULTS OF PRELIMINARY PARAMETER SCREENING

Analysis of the results based on the nine response equations generated revealed that four of the fourteen parameters studied were the most influential within the ranges studied. These parameters are: aeration, $ZnSO_4$, KCN and Cu flotation pH.

Aeration was found to positively affect recovery of both copper and zinc and also grade of both concentrates. It improved selectivity between Cu and Zn and also between Zn and Fe. This effect is shown in fig. 4.1.

The level of SO_2 used at this screening stage was found to be too low to show any effect. It was decided to include it in the final design.

4.3. RESULTS OF FINAL EXPERIMENTAL DESIGN AND INTERPRETATIONS

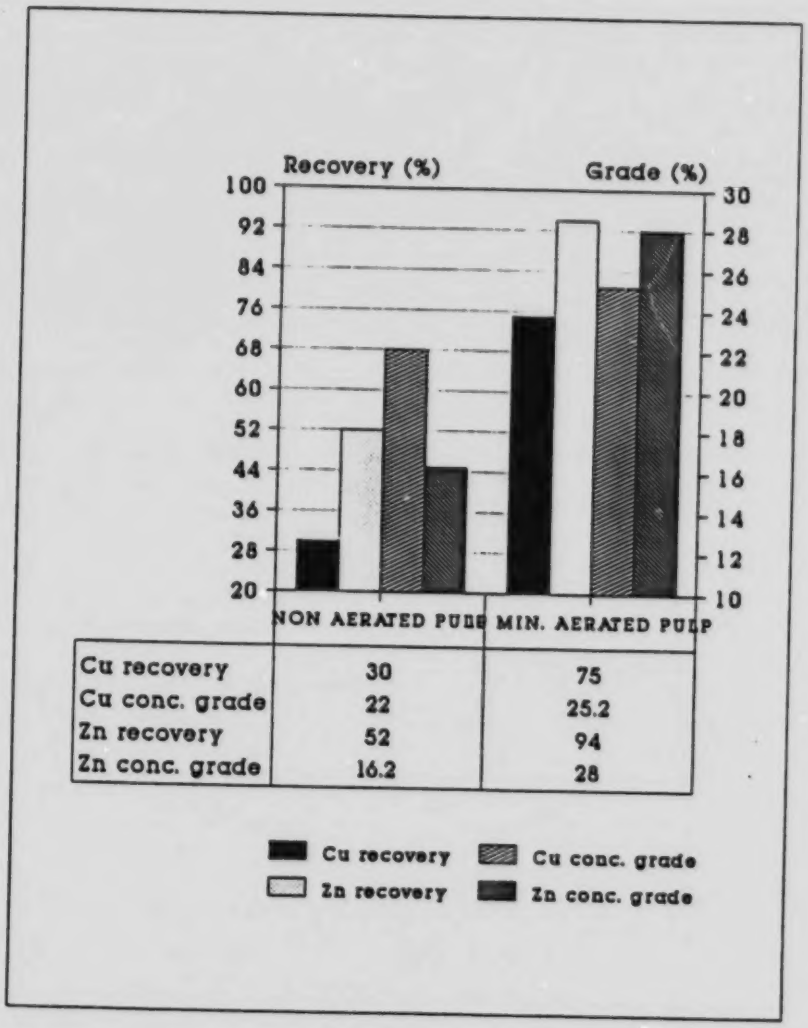
Since it became evident that aeration is absolutely necessary to achieve an acceptable selectivity between Cu and Zn, aerated pulp and monitoring of the pulp potential became the focus of the final study.

Table 4.1. Box-Behenchen 4-factor experimental design.

LEVEL	-Alpha	-1	0	+1	+Alpha
$ZnSO_4$ (g/t)	0	130	390	650	780
KCN (g/t)	0	55	165	275	333
CaO (g/t)	0	111	333	555	666
SO_2 (g/t)	0	222	666	1110	1332

The final design used was the 4 factor Box-Behenchen central composite design which requires 25 experiments plus 3 centre point replications. The four factors were $ZnSO_4$, KCN, CaO and SO_2. Cu and Zn were floated at a pH value of 8 and 10 respectively. The levels of each

Figure 4.1A. The Effect of 10 minutes aeration of flotation pulp on the major process responses.



	NON AERATED PULP	MIN. AERATED PULP
Cu recovery	30	75
Cu conc. grade	22	25.2
Zn recovery	52	94
Zn conc. grade	16.2	28

of the factors is given in table 4.1 and the ranges are set based on the results of the response analysis during the screening stage.

Aeration required more attention and it was decided to investigate its effect separately. All the other parameters were fixed at the level which was found, during screening, to affect the overall result positively. The fixed values of these parameters are as follows:

A. Copper flotation:

pulp aeration time	20 min
pH	8
KAX	22.2 g/t
MIBC	4.4 g/t
conditioning time	3 min.
flotation time	6 min

B. Zinc flotation:

pH	10
$CuSO_4$	150 g/t
activation time	3 min
NaEtX	167 g/t
MIBC	11.1 g/t
conditioning time	3 min
flotation time	10 min

OPTIMIZATION CRITERIA

The optimum conditions were determined by the multiple response optimization techniques based on the following criteria:

R2 - maximum Cu recovery to Cu rougher tail	10% of the feed
R3 - minimum zinc recovery	87%
R4 - maximum Zn recovery to Cu concentrate	7%
R5 - minimum Cu selectivity against Zn $(SI)_{Cu/Zn}$	0.85
R6 - minimum rougher Cu concentrate grade	22%
R7 - minimum Cu selectivity against Zn $(SI)_{Cu/Fe}$	0.88
R8 - minimum Cu selectivity against Zn $(SI)_{Zn/Fe}$	0.78
R9 - maximum Zn content of the rougher Cu con	4%

Two tests (see Table 4.2 and Table 4.3) were conducted at two different optimum conditions (Point "A" and Point "B" in Figure 4.2) to validate the two delineated optimum regions. As indicated, the results fall within the required ranges confirming the validity of the statistical analysis. The selectivity is excellent particularly for the test conducted at point "B". Note the exceptionally high grade and high recovery of Cu with the rougher concentrate grading only 2.4% Zn at 92.6% Cu recovery.

Table 4.2. Results of a flotation test conducted at point A within the optimum region (figure 4.2A).

Product	wt%	Assay		cum. grade		cum. recovery		SI
		% Cu	% Zn	% Cu	% Zn	Cu (%)	Zn (%)	
feed	100	2.59	3.62	2.59	3.62	100.0	100.0	-
2' Cu con	7.78	26.42	2.37	26.42	2.37	79.4	5.1	0.94
4' Cu con	1.49	12.81	4.87	24.23	2.77	86.8	7.1	0.92
6' Cu con	0.91	7.38	5.91	22.73	3.05	89.3	8.6	0.90
8' Cu con	0.57	5.75	6.89	20.45	3.26	90.6	9.7	0.89
2' Zn con	6.20	1.52	40.34	1.52	40.34	3.6	78.4	
4' Zn con	1.38	1.98	10.81	1.60	35.00	4.7	83.1	
6' Zn con	1.23	1.49	3.70	1.59	30.59	5.4	84.5	
10' Zn con	1.19	1.30	2.33	1.55	27.23	6.0	85.4	
Tail	79.30	0.10	0.15	0.10	0.15	3.7	4.1	

Table 4.3. Results of a flotation test conducted at point B within the optimum region (figure 4.2A).

Product	wt%	Assay		cum. grade		cum. recovery		SI
		% Cu	% Zn	% Cu	% Zn	% Cu	% Zn	
feed	100	2.54	3.06	2.54	3.06	100.0	100.0	-
3' Cu con	6.4	28.6	1.6	28.6	1.6	72.1	3.4	0.95
5' Cu con	1.9	22.5	3.9	27.2	2.2	88.9	5.8	0.93
7' Cu con	0.7	13.4	5.7	26.0	2.4	92.6	7.1	0.92

Figure 4.2A. Locations of the optimum regions and validation test points "A" and "B".

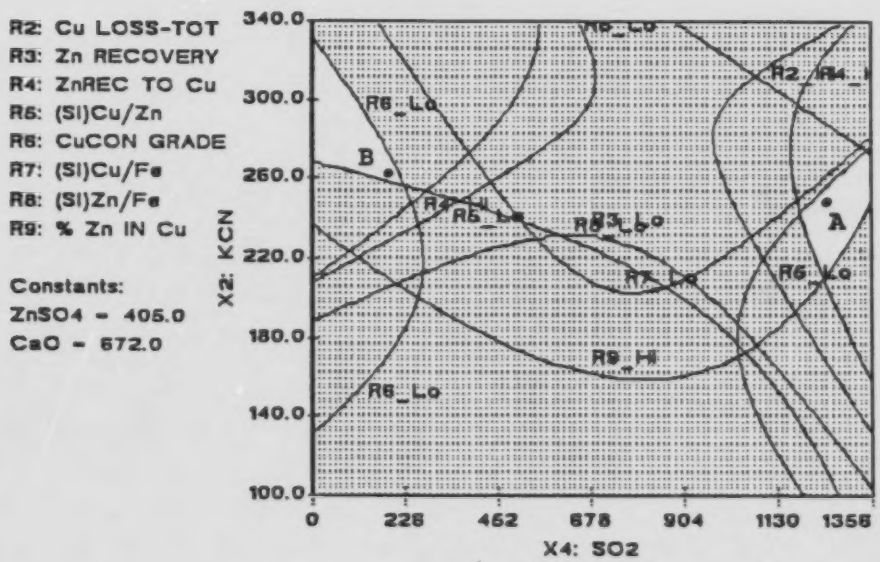
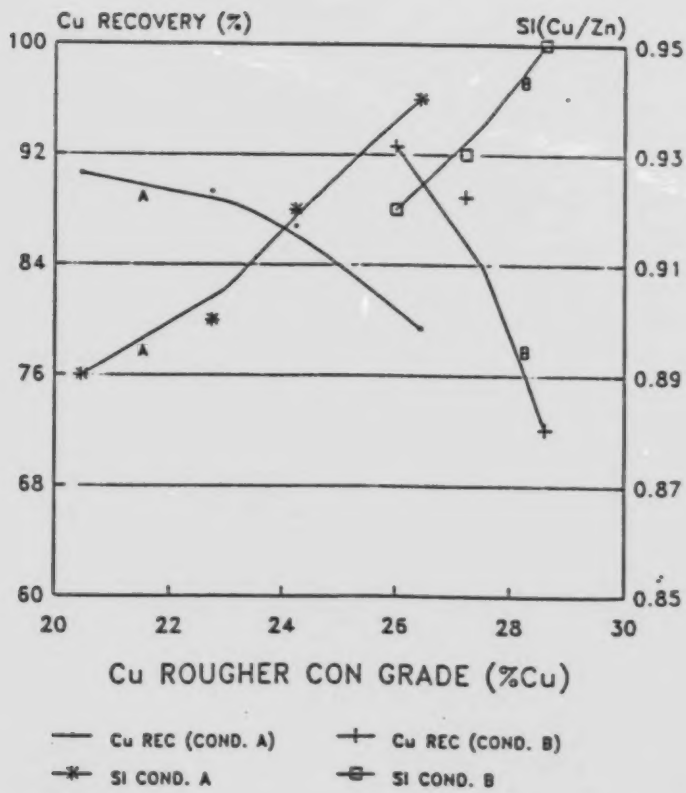


Figure 4.2B. Comparison of the two conditions "A" and "B".



In accordance with the predicted values the recovery of each metal to its respective concentrate is very high and the recovery of Zn to Cu con is quite low and also Cu rougher concentrate grade is very high. The rougher copper concentrate grade (26% Cu and 2.6% Zn) obtained under condition "B" of Figure 4.2A is much better than the final Cu concentrate produced by the plant (24.4% Cu and >5% Zn) after double cleaning. The result obtained under condition "A" indicates that it is possible to produce a rougher copper concentrate of 24.23% Cu and 2.77% Zn at 86.8% Cu recovery and 88.0% Zn recovery to their respective rougher concentrates. Cleaning of the rougher Cu concentrate may reduce Zn loss to Cu concentrate by half, thus insuring a Zn recovery of about 90% while obtaining a very high grade (>26%) Cu concentrate at a recovery of about 85%.

4.3.1 EFFECT OF THE PARAMETERS ON Cu AND Zn ROUGHER CONCENTRATE GRADES AND RECOVERY

$ZnSO_4$ and KCN

The selectivity of Zn depression against Cu was found, as expected, to depend on the ratio of $ZnSO_4$ to KCN.

- At all levels of KCN, there exists one level of $ZnSO_4$ at which a maximum selectivity can be achieved. This level is about 3 mole/ton of $ZnSO_4$ (fig. 4.3, 4.4, and 4.5). The reason why Cu is also depressed above this dosage is not clear.

- At all levels of $ZnSO_4$ (0 to 5 mole/t), the selectivity of Zn depression against Cu increases with an increase in KCN level up to 5 mole/t. In the absence of CaO, however, the selectivity decreases with an increase in KCN beyond 1 mole/t (fig. 4.5).

- $ZnSO_4$ was found to have no significant effect on Zn concentrate grade while at a level lower than 3 mole/t it increased Cu concentrate grade. When this level is exceeded Cu concentrate grade decreases.

- KCN up to 200 g/t increased Cu concentrate grade. When this level is exceeded it begins decreasing Cu concentrate grade. The reason seems to be not much due to depression of chalcopyrite but due to pyrite flotation at lowered pulp potential (see fig. 4.9). KCN increases Zn concentrate grade almost under all conditions studied, because much of the pyrite which usually floats with sphalerite already floated with chalcopyrite.

CaO

CaO was also found to have a positive effect both on the concentrate grade and recovery of Cu and Zn. The general trend (fig. 4.6 a & b) is that with an increase in CaO addition, the recovery of Cu to Cu con and of Zn to Zn con increases at all levels of SO_2 and KCN. From fig. 4.6 it is clear that the optimum CaO dosage has not yet been reached.

SO_2

SO_2 at a level lower than 666 g/t decreases Cu concentrate grade by reducing the pulp potential which leads to Cu depression. At a level higher than 1000 g/t, however, it begins increasing the Cu concentrate grade by "activating" chalcopyrite (cleaning the tarnished surface). SO_2 generally increased Zn rougher concentrate grade.

SO_2 was found to have different effects on chalcopyrite and sphalerite under different conditions. Its role as a sphalerite depressant during Cu rougher flotation was observed to be diminishing with an increase in cyanide.

Figure 4.3. Effect of KCN to ZnSO4 molar ratio on Cu/Zn selectivity in the presence of CaO and SO_2.

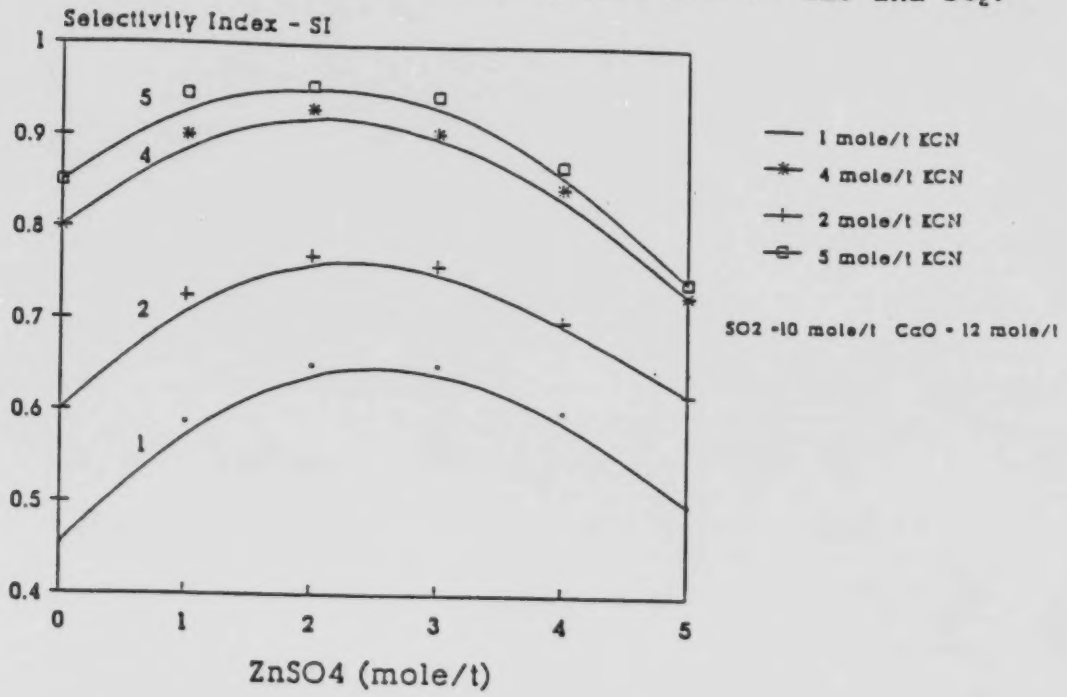
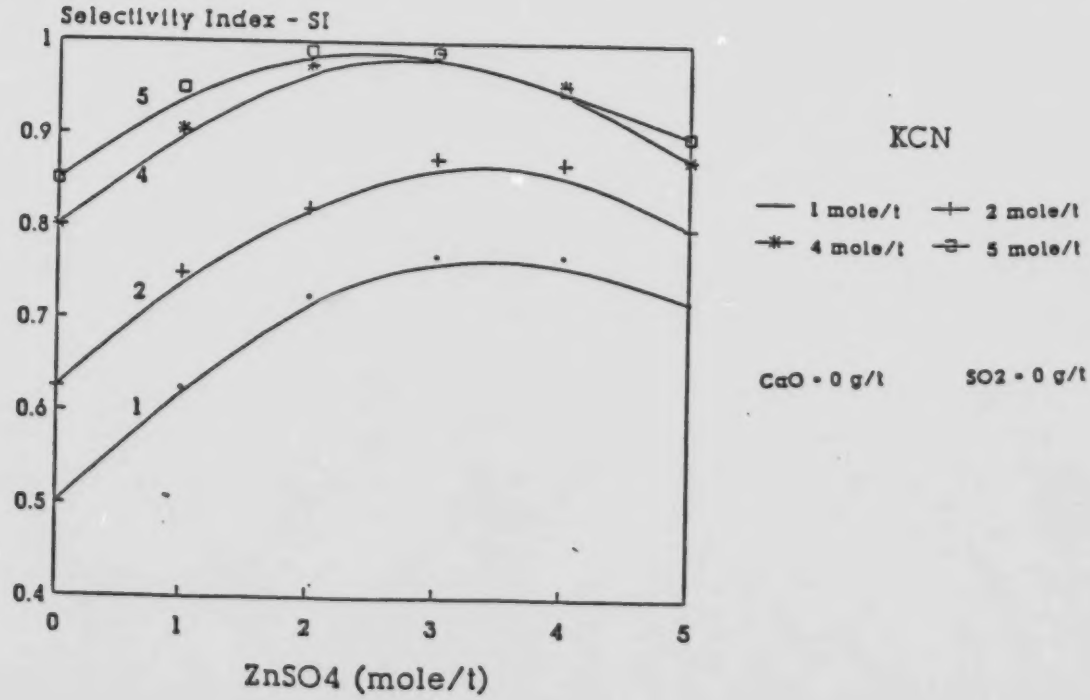


Figure 4.4. Effect of KCN to ZnSO4 molar ratio on Cu/Zn selectivity in the absence of CaO and SO_2.



In the absence of CaO and KCN (fig. 4.7), both of which reduce the pulp potential, SO_2 increases Zn recovery to Zn rougher concentrate from about 60% to 95%, while decreasing Cu recovery from 92% to 83%. In other situations, as for example in fig. 4.8, SO_2 increases Cu/Zn flotation selectivity as observed by the increase in recovery of both metals to their respective rougher concentrates. In other cases, where the combination of all four depressants was used (fig. 4.9, 4.10) SO_2 consistently increased copper recovery while its effect on Zn remained almost insignificant. This varying effect is due to the changes in pulp potential brought about by SO_2 addition at varying levels of other potential determining species.

Figure 4.5. Effect of KCN to ZnSO4 molar ratio on Cu/Zn selectivity in the absence of CaO and presence of SO_2.

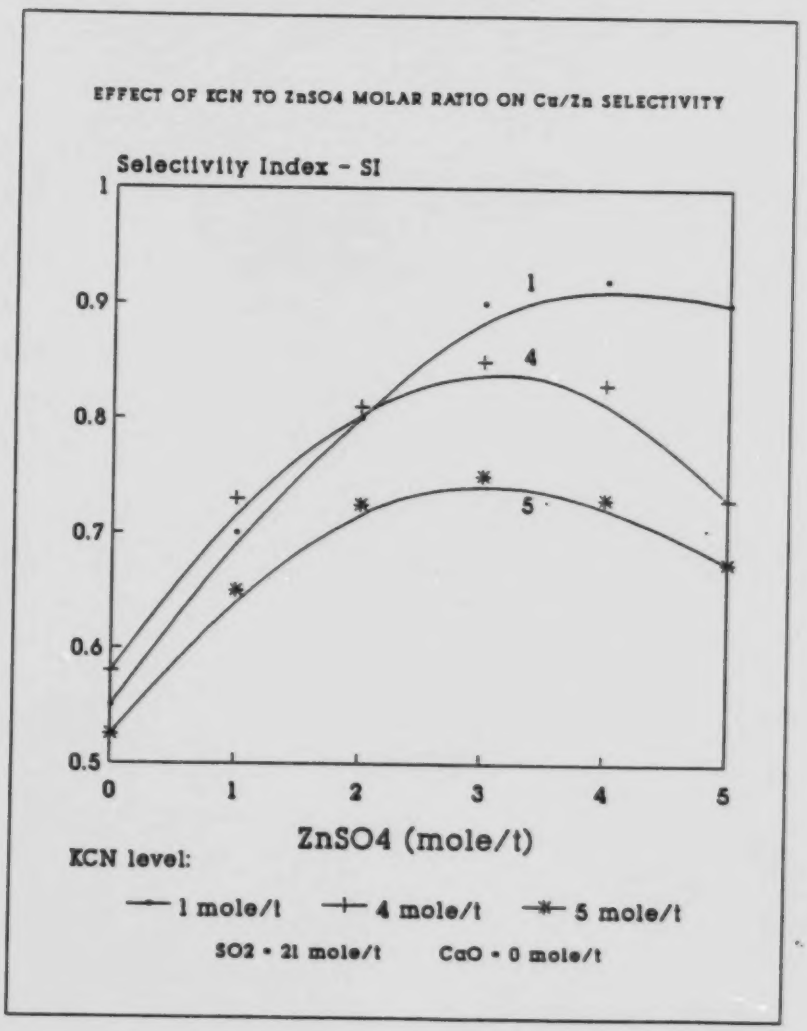


Figure 4.6A

Effect of CaO on Cu/Fe selectivity.

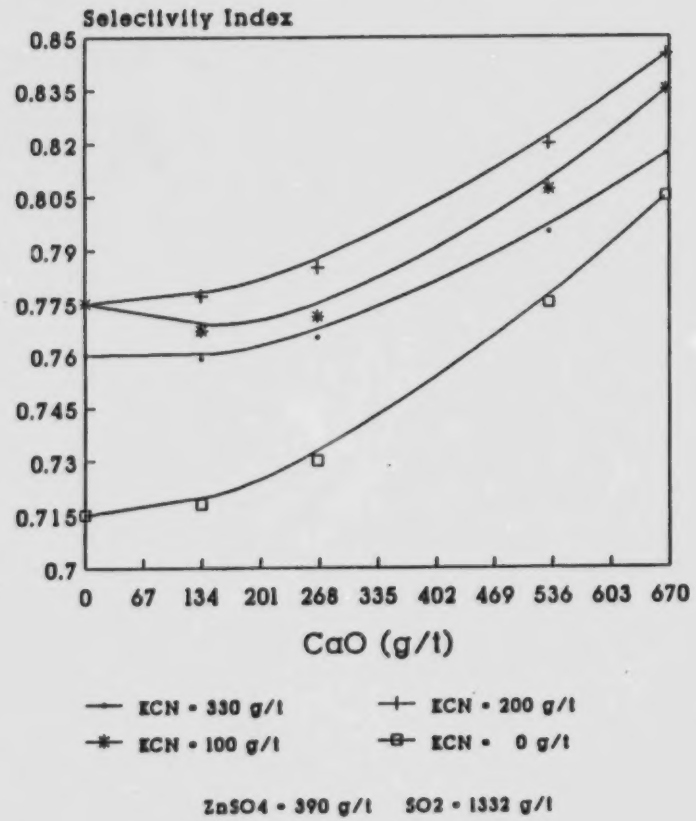


Figure 4.6B

Effect of CaO on Cu and Zn recovery.

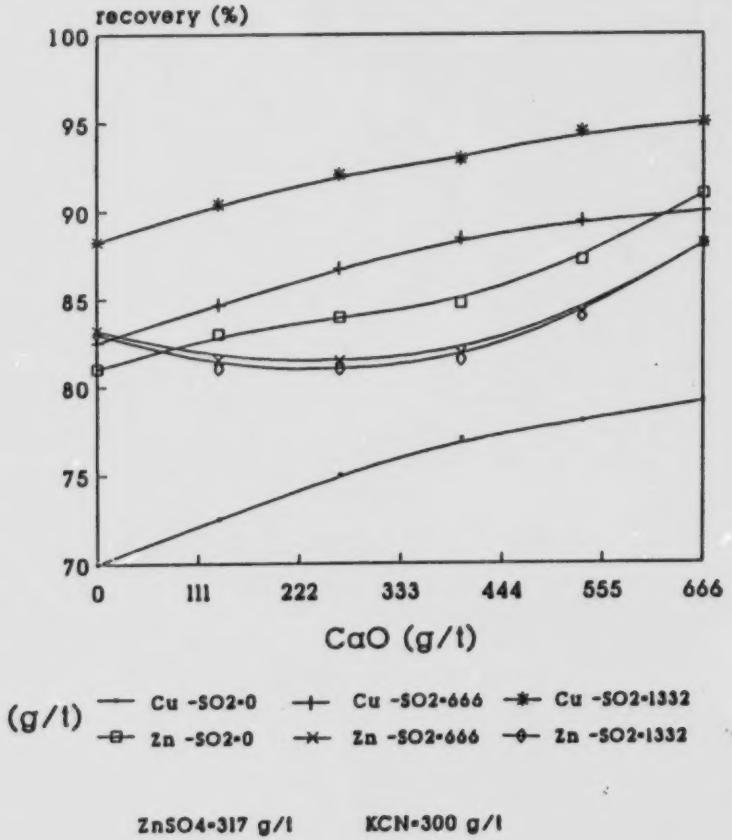
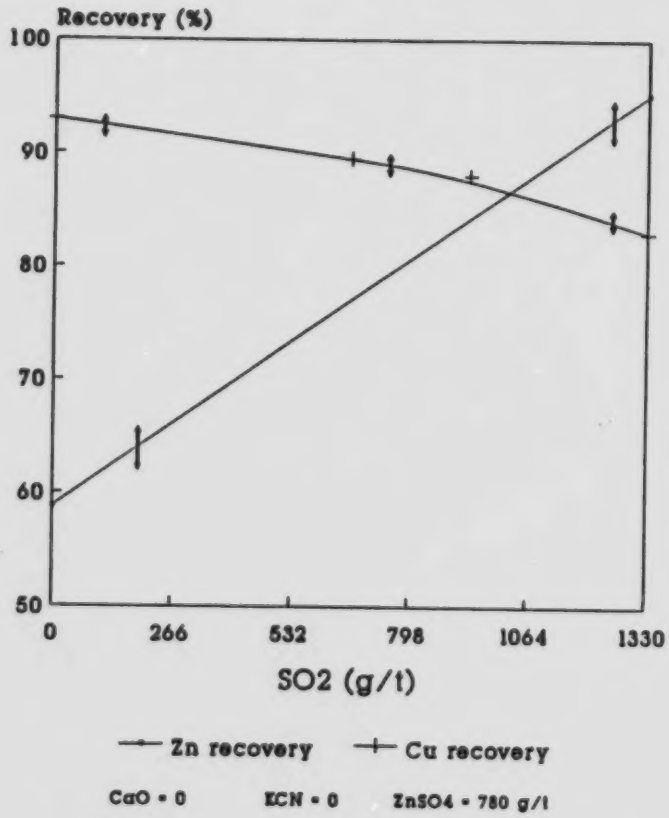


Figure 4.7

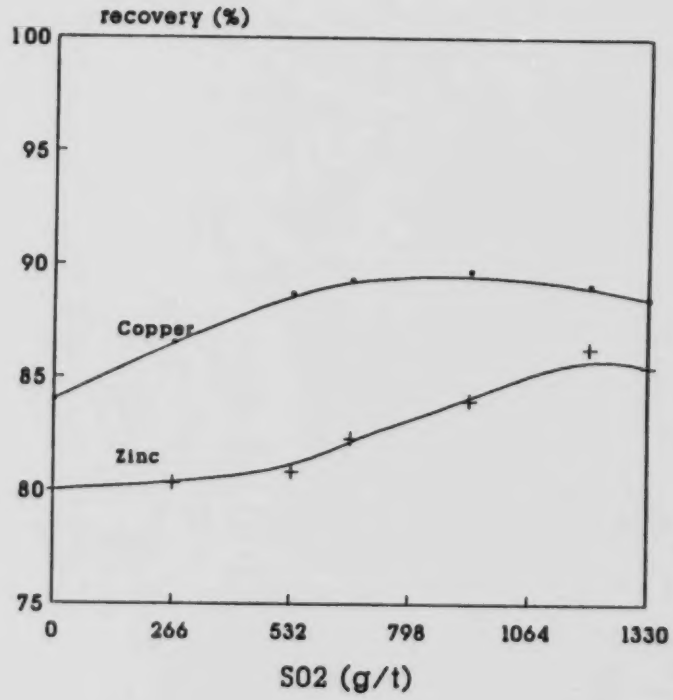
EFFECT OF SULPHUR DIOXIDE ON Cu & Zn (ROUGHER) RECOVERIES



CaO = 0 ECN = 0 ZnSO4 = 780 g/t

Figure 4.8

EFFECT OF SULPHUR DIOXIDE ON Cu/Zn FLOTATION SELECTIVITY



ZnSO4=390 g/t ECN=165 g/t CaO=666 g/t

Figure 4.9

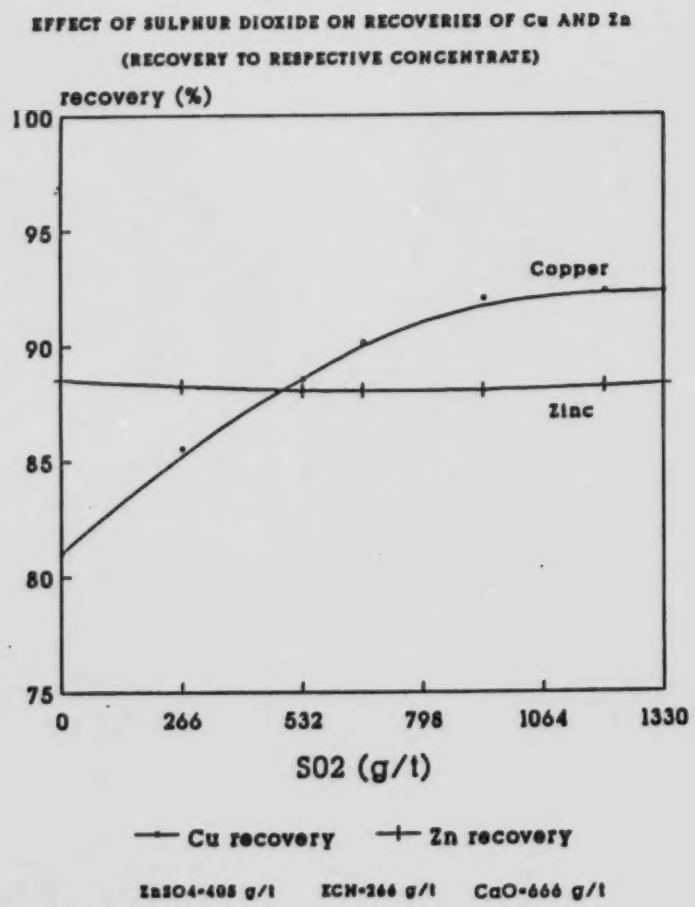
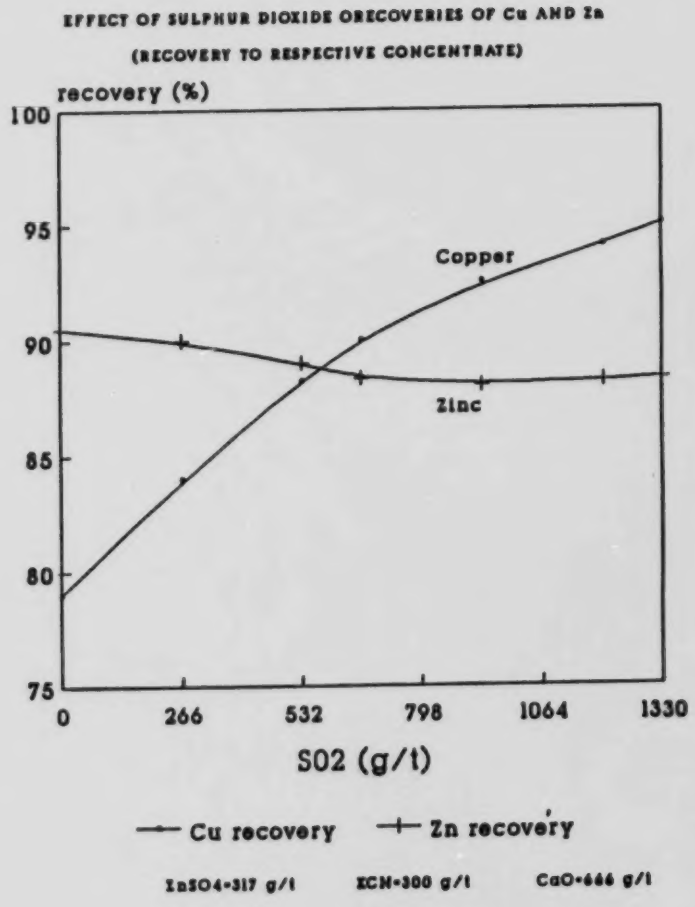


Figure 4.10



4.4.0 THE EFFECT OF PULP POTENTIAL ON Cu/Zn, Cu/Fe AND Zn/Fe SELECTIVITY

A considerable amount of work has been done during the present study to establish a correlation between aerated pulp potential, modifiers and flotation selectivity. The pulp potential was determined with a platinum electrode as an indicator and saturated calomel electrode as a reference electrode. The measured potential was not converted to the standard hydrogen electrode scale and is designated as E_p.

The correlation between flotation response and the aerated pulp potential after the addition of collector, frother, and sphalerite activator was observed to be very weak. It is the pulp potential just before collector addition that determines the selectivity between individual sulphide mineral separations, not only during the primary stage of selective flotation (Cu from Zn & Fe) but also during subsequent secondary flotation (Zn from Fe). Since there was no reagent introduced during the pulp measurement no difficulties were encountered in obtaining consistent data.

The potential developed after 20 minutes pulp aeration was investigated and was found to vary with the levels of each of the depressants used (fig. 4.11).

An increase in a level of KCN and CaO addition to the grinding mill makes the flotation pulp more reducing after 20 min. aeration regardless of the amount of SO_2 added. However, increasing the SO_2 makes the pulp less reducing at all levels of KCN and CaO added. This clearly indicates that KCN, SO_2 and CaO all have a potential controlling role which is rarely taken into consideration during their application in sulphide flotation. Thus, in sulphide flotation, whenever the SO_2 and CaO or SO_2 and KCN combination is used an interactive effect should be expected and this effect should be evaluated.

Four flotation tests at different potentials prior to chalcopyrite hydrophobization were conducted with a combination of depressants which had been identified as giving a high selectivity. The test conditions are the same as those used to verify the validity of the optimum region shown in figure 4.1A. The low Zn concentrate grade is due to the prolonged flotation time. The interpretations are presented in fig. 4.12 to 4.13.

One of the phenomena worth noticing is that the depressive action on chalcopyrite and sphalerite of these reagents is very strong in an oxygen deficient pulp (-283 mV in fig. 4.12A and 4.12B). On the other hand, the same combination of depressants at the same level gives the highest recovery of both minerals to their respective concentrates when the pulp is sufficiently oxidized (-119 mV in fig. 4.12) as a result of 20 min aeration, all other conditions remaining the same. The conclusion is that the evaluation of these depressants should always be on the

Figure 4.11. Pulp potential variation with depresssants after 20 minutes aeration.

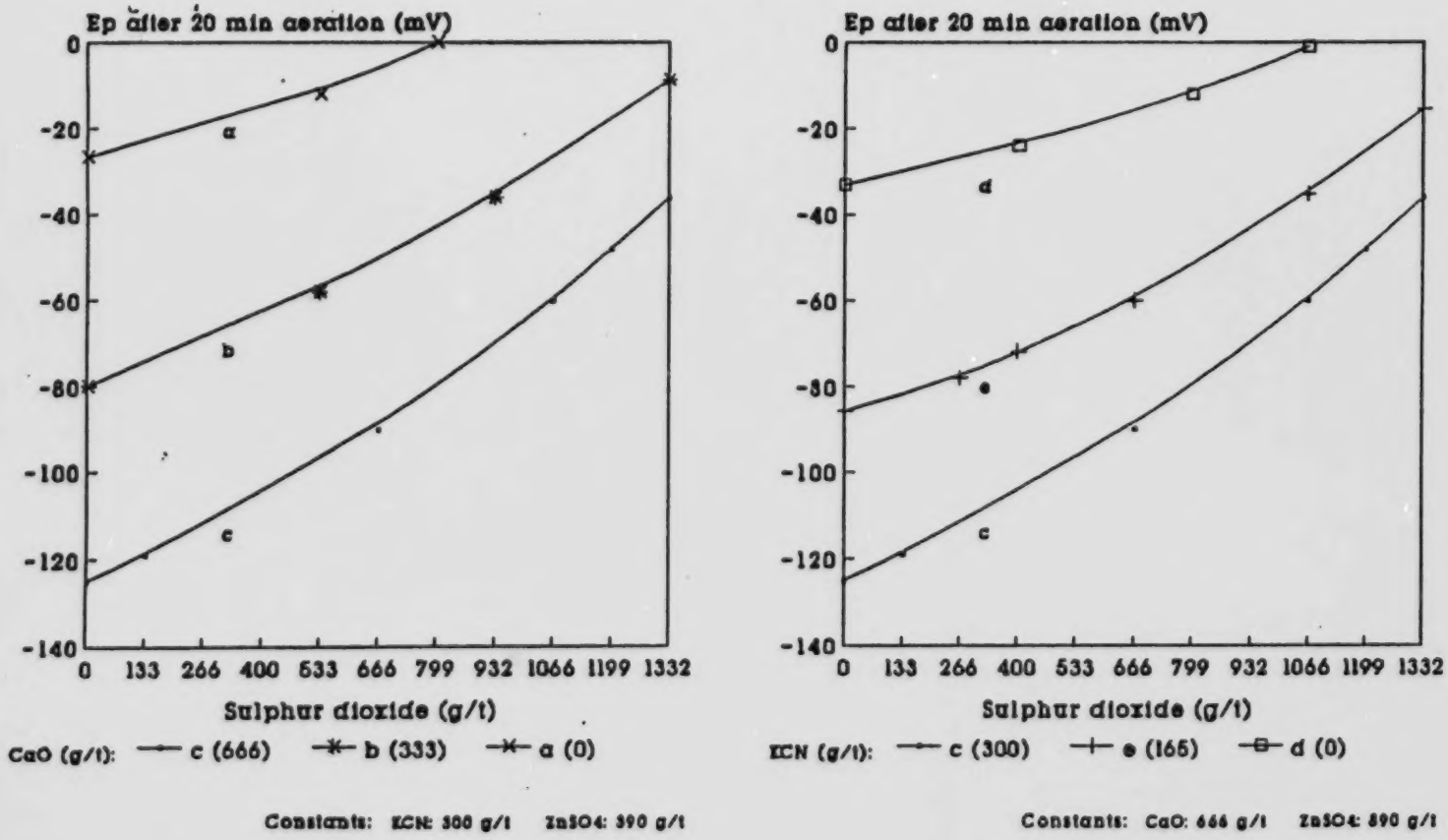


Figure 4.12A

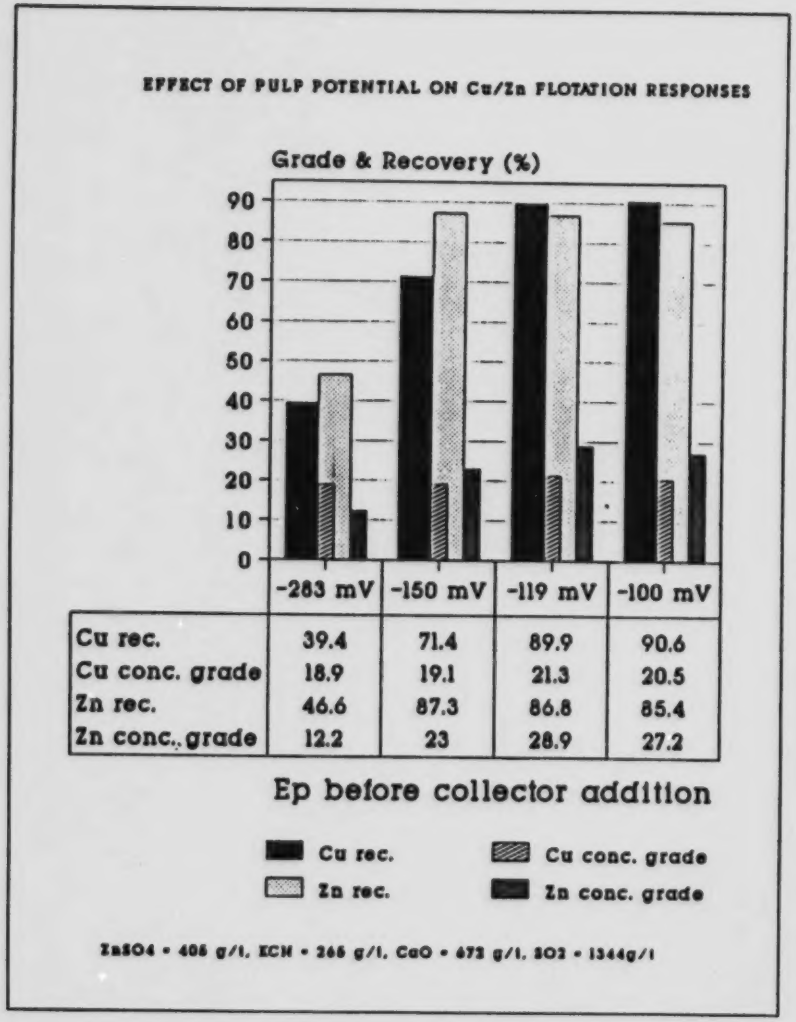
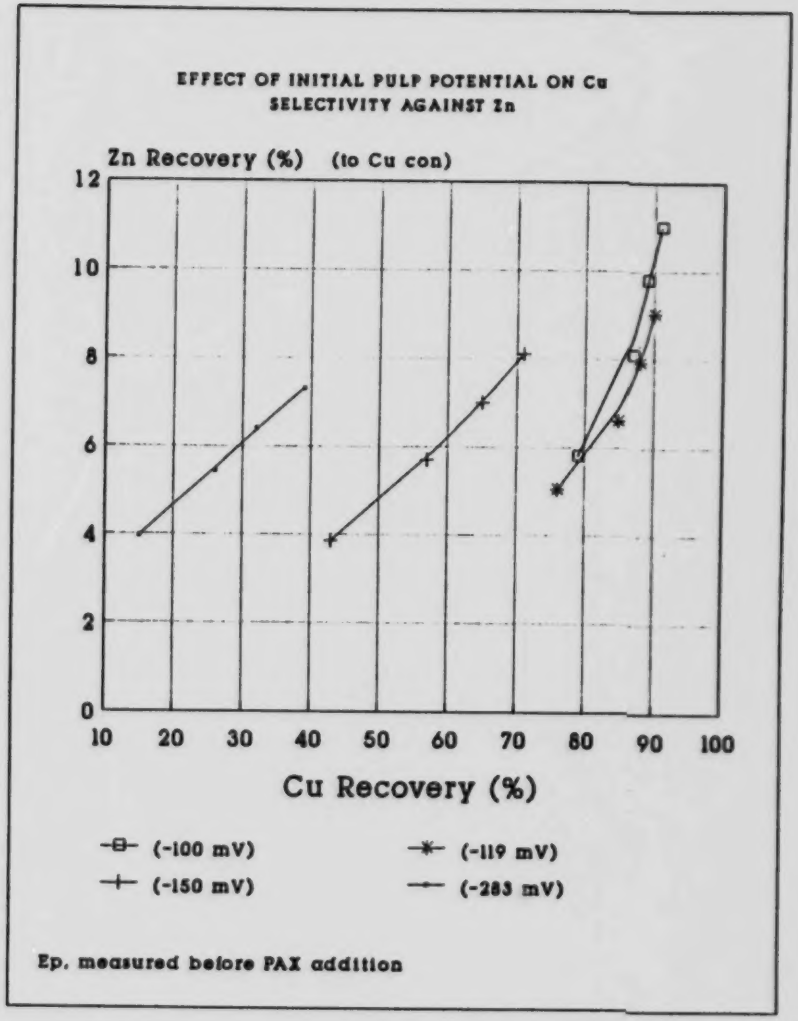


Figure 4.12B



basis of the mixed redox potential developed due to the grinding atmosphere and the introduction of the depressant(s).

In fig. 4.12A and 4.12B, the adjustment of the pulp potential alone (from -283 mV to -119 mV) improved Cu and Zn recovery from 38% and 45% to 90 and 86% respectively. The grade of Cu concentrate improved from 19% to 23% while that of Zn concentrate increased from 12% to 28%. Though this flotation condition is the most selective condition, without the adjustment of pulp redox potential (by aeration in this case) it would have been rejected as ineffective.

The results of timed (8 minutes) Cu flotation at different pulp potentials (measured before collector addition) is presented in fig. 4.13. The selectivity of the non aerated pulp (-283 mV) increases with flotation time (contrary to normal flotation behaviour) (see also fig. 4.13A and 4.13B) but in general it is very low compared to the selectivity of the aerated pulp. As the flotation time increases the pulp redox potential becomes more oxidizing "activating" chalcopyrite and depressing sphalerite and pyrite (increasing concentrate grade). This can be observed from the shape of the grade-recovery curves in fig. 4.13a and 4.13b (flotation at -283 mV) in which the recovery and grade of both Cu and Zn all increase at the same time. This can also be used to judge whether aeration or pulp oxidation by other means is required or not.

It seems very important to define an Ep of maximum selectivity if it has to be used as an effective control parameter. The highest selectivity between Cu & Zn is achieved at a potential of about -119 mV (fig. 4.12A and 4.12B). An increase in redox potential beyond -119 mV decreases both selectivity and recovery and grade of both metals. However, an increase in potential to -100 mV does not significantly decrease Zn recovery while there is an insignificant increase in Cu recovery. This indicates that there is a wide range of redox potential value for manoeuvring and within this range (around -110 mV(SCE)) the process is not sensitive to minor changes. Ten minutes of intensive aeration was required to raise the pulp potential from -119 mV to -100 mV.

In a somewhat similar study Beyzavi and Kitschen (31) showed that the adjustment of Eh after the addition of reagents before Cu flotation improves selectivity. Though the approaches and the pulp pretreatment procedures in their study and our study are different, the conclusion that the pulp redox potential determines selectivity, recovery and grade is identical. Since their study is based on Cu/Pb/Zn ores (pyrrhotite as a major gangue sulphide) and our study is based on pyritic Cu/Zn ore it can be assumed that it is a general phenomenon for all sulphide ores.

Figure 4.13A

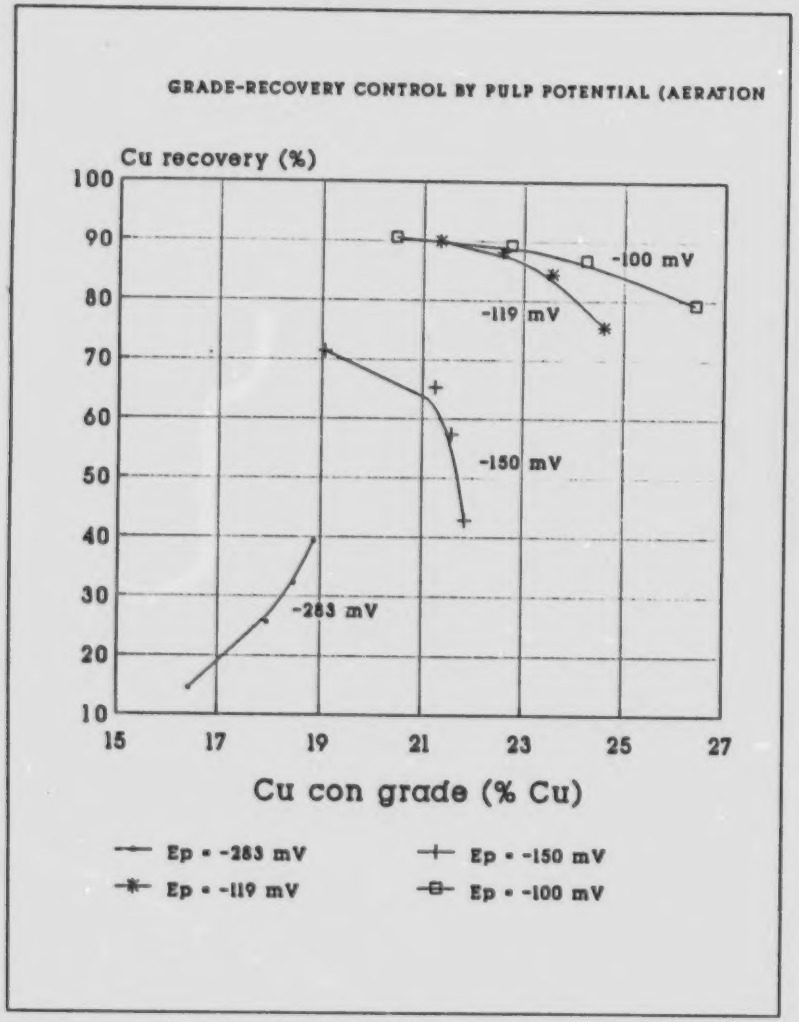
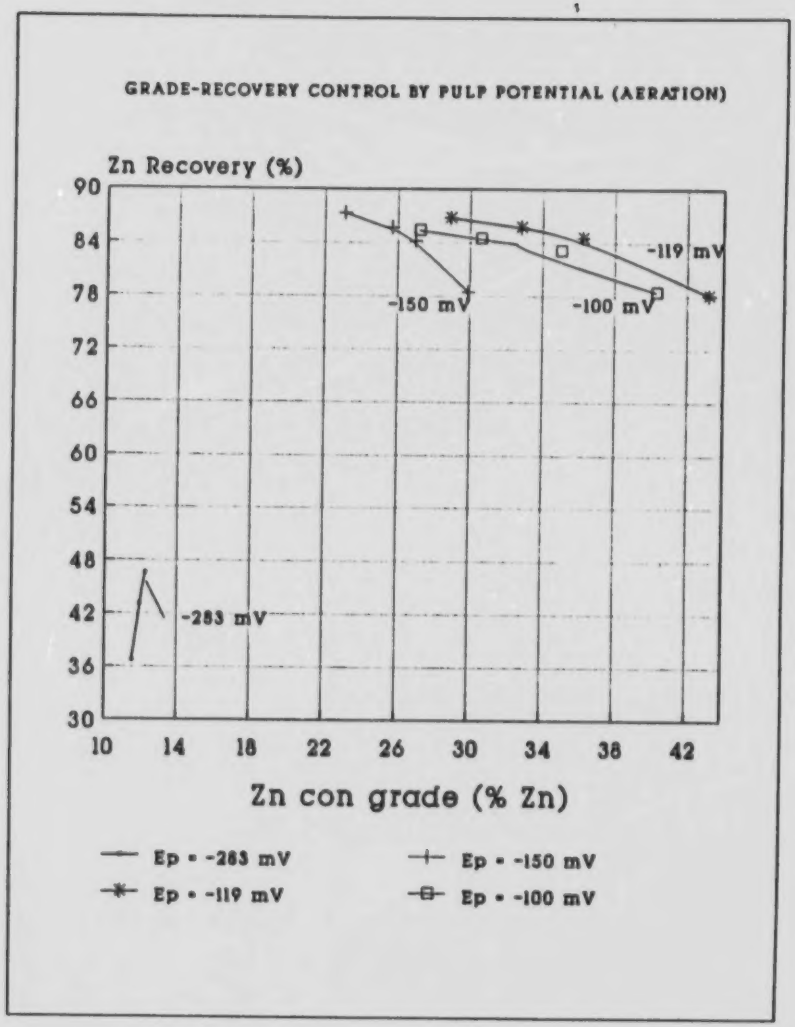


Figure 4.13B



The fact that the flotation responses and selectivity are determined by the pulp potential just before collector addition (depressants having been added during grinding) has very important implications for industry. The recycled water, which usually changes the potential of fresh pulp, may be used at any point after the pulp has been conditioned with collector but not before that. This has to be always taken into consideration if potential is to be used as a process control parameter.

5.0 CONFIRMATORY TEST ON ANOTHER ORE

The conditions which permitted a good selective separation of Cu against Zn from the Trout Lake ore were tested on the Kidd Creek ore with a similar Cu to Zn head grade ratio. About 90% Cu was recovered at a rougher concentrate grade of 23.2% Cu and only 2.4% Zn. The concentrator produces a Cu concentrate grading 25% Cu with more than 3% Zn after roughing, regrinding, scavenging and triple cleaning (at about the same recovery). The two concentrators of the two ores chosen are using entirely different circuits, different grind size and different main reagents. Nevertheless, our scheme has been found to work equally good for both ores at the same grind. The test work result for the Kidd Creek ore is given in table 5.1.

Table 5.1. Confirmatory testwork result (Kidd Creek ore).

PRODUCT	WEIGHT g	WEIGHT %	ASSAY %Cu	ASSAY %Zn	RECOVERY % Cu	RECOVERY % Zn	SI
1. Cu CON	64.00	7.16	27.26	1.55	70.34	2.50	
2. Cu CON	19.90	2.23	18.14	3.53	14.55	1.77	
3. Cu CON	11.10	1.24	9.16	5.54	4.10	1.55	
CUMULAT.	95.00	10.63	23.23	2.43	88.99	5.83	0.934
1. Zn CON	34.40	3.85	1.16	60.95	1.61	52.94	
2. Zn CON	23.70	2.65	1.77	44.56	1.69	26.66	
3. Zn CON	27.80	3.11	1.75	11.79	1.96	8.28	
CUMULAT.	85.90	9.61	1.52	40.52	5.26	87.87	
TAIL	712.50	79.75	0.20	0.35	5.75	6.30	
HEAD-CALC	893.40	100.00	2.78	4.43	100.00	100.00	

6.0 CONCLUSIONS AND RECOMMENDATIONS

The main non-mineralogical factors that affect Cu and Zn flotation selectivity during complex sulphide flotation are the quantity and type of reagents added to the system at the early stage of grinding and the level of pulp potential developed during grinding and conditioning.

Sphalerite floats with chalcopyrite mainly because it is activated by heavy metal ions, particularly Cu ions, and its surface behaves similarly to that of a copper sulphide mineral (34,40). It may also float due to favourable pulp redox potentials that allow the formation of elemental sulphur on the surface. The other reason is the dissolution of lattice Zn ions forming a Zn deficient sphalerite surface rich in sulphur ions; such a surface is hydrophobic and can also be easily activated by heavy metal ions (40,41). Thus selective flotation of complex sulphide minerals requires strictly controlled grinding conditions and a careful manipulation of pulp electrochemistry during conditioning.

It is virtually impossible to find a single reagent which can effectively depress one sulphide mineral and at the same time activate the other(s) (or at least remain neutral) to facilitate an acceptable selective flotation. Nevertheless, the result of the present work demonstrates that it is possible to create conditions that are "activating" for chalcopyrite and depressing for sphalerite and pyrite by combining more reagents and regulating the pulp electrochemistry.

Identification of conditions of maximum selectivity is possible through a carefully engineered strategy and once these reagent conditions are determined the control of grade and recovery becomes much easier. The use of powerful statistical software packages can make this task even simpler.

Zinc sulphate, cyanide, sulphur dioxide and lime were found to form a combination that can provide proper depression and can create a proper pulp redox potential (after aeration) to allow highly selective separation of Cu from Zn and Fe. The reason for their efficiency is due to their following specific characteristics:

(a) $ZnSO_4$ prevents the dissolution of lattice zinc ions whose space can then easily be occupied by a copper ion from pulp leading to sphalerite activation (39, 43).

(b) Cyanide complexes the activating Cu ion on the sphalerite surface, and also complexes free Cu and other heavy metal ions in the pulp (39),

(c) CaO creates the alkalinity required to depress iron sulphide gangue minerals and also to a degree sphalerite (20),

(d) SO_2 or sulphite ion complexes the surface elemental sulphur that makes sphalerite and other iron sulphide minerals float with chalcopyrite (3,4). It limits collector adsorption by control of the redox potential (20) and it may also form insoluble metal sulphite compounds (20) on pyrite and sphalerite surfaces, reducing their floatability. In the presence of Ca ion, it also forms hydrophillic calcium sulphite coatings on the minerals.

Our results indicate that not only is the proper combination of modifiers important to obtain acceptable selectivity but also the pulp potential developed as a result of their interaction. Aeration of flotation pulp (and thus adjustment of the highly reducing pulp potential developed during grinding in a steel mill) prior to copper hydrophobization was found to play a dominant role in determining the selectivity of copper against zinc and iron, and subsequently of zinc against iron.

If the effect of each reagent on the pulp potential is evaluated and the optimum flotation condition based on this evaluation is determined, then pulp potential may be used as a process control mechanism. A thorough investigation of this potential in flotation may require a systematic evaluation of specific conditions such as: (a) nature of grinding- proximity and duration of galvanic contact (grinding and conditioning time); (b) relative surface area of the sulphide minerals present in the pulp; (c) preaeration or no aeration; (d) nature of the minerals with respect to conductivity; (e) pH; (f) agitation speed; (h) the presence and absence of other redox species, (i) pulp density, and (j) reagent concentrations etc.

Two ore samples (from two different sources), which are currently treated under entirely dissimilar flotation and reagent schemes, responded similarly to the scheme developed during the current investigation. It seems, at this stage, that an adoption of a generalized flotation flowsheet for an effective separation of chalcopyrite from sphalerite could be possible. Verification of this and continuous testing (piloting) of the process will be required (II. phase of this study).

Though the bench-scale selectivity control strategy used in this investigation has not yet been piloted, the process may provide a very high grade rougher copper concentrate (>23% Cu) with low Zn content (<2.7%) at higher than 87% Cu recovery. The recovery of Zn to the Zn rougher concentrate would be higher than 89%.

Currently, the concentrator which treats the ore used for the original investigation produces a Cu concentrate with 23.4% Cu and higher than 5% Zn after double cleaning (at a significantly lower recovery). The other concentrator which treats the ore sample used for the confirmatory test produces a higher grade Cu concentrate (25-27% Cu) with 4 to 5% Zn after triple cleaning.

The results achieved are, thus, very encouraging and more work to define the correlation between the specific electrochemical conditions and flotation selectivity are strongly recommended. The process has to be tested for other ores, and locked cycle tests have to be conducted (before piloting) to identify potential problems.

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